STABILIZATION OF LOWER OXIDATION STATES OF MOLYBDENUM BY REDUCTIVE NITROSYLATION USING HYDROXYLAMINE IN AQUEOUS - AEROBIC MEDIUM

A Thesis Submitted
in Partial Fulfilment of the Requirements
for the Degree of
DOCTOR OF PHILOSOPHY

By

PERIYASAMY SUBRAMANIAN

to the
DEPARTMENT OF CHEMISTRY
INDIAN INSTITUTE OF TECHNOLOGY, KANPUR
MAY 1981

To my thesis supervisor
Sabyasachi Sarkar

and

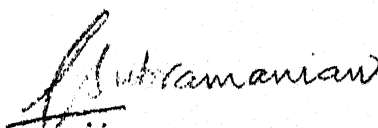M.Sc. Teachers
V.V. Ramanujam and J.D. Koola

One might think of the evolutionary process
passing through three distinct phases   of
chemistry. Inorganic chemistry to organic
chemistry and organic chemistry to   biolo-
gical chemistry. And it is true   that   if
organic chemist is familiar with the wonders
undreamed of by the inorganic chemist , the
wonders can be visualised by the biochemist
in his daily tasks, which stagger the imagi-
nation and sharpen the envy of the   organic
chemist.

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– S. MORGULIS

</div>

STATEMENT

I hereby declare that the matter embodied in this thesis is the result of investigations carried out by me in the Department of Chemistry, Indian Institute of Technology, Kanpur, India, under the supervision of Professor Sabyasachi Sarkar.

In keeping with the general practice of reporting scientific observations, due acknowledgement has been made wherever the work described is based on the findings of other investigators.

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CERTIFICATE

Certified that the work contained in this thesis entitled, "STABILIZATION OF LOWER OXIDATION STATES OF MOLYBDENUM BY REDUCTIVE NITROSYLATION USING HYDROXYLAMINE IN AQUEOUS – AEROBIC MEDIUM" has been carried out by Mr. Periyasamy Subramanian, under my supervision and the same has not been submitted elsewhere for a degree.
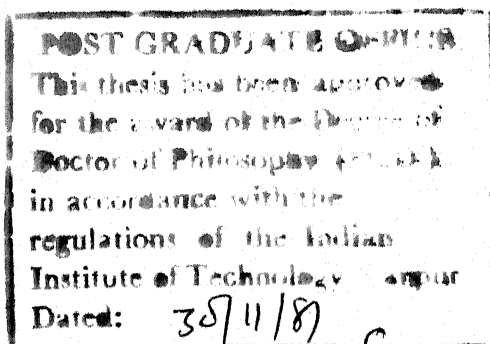
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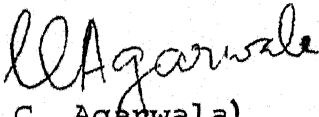
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DEPARTMENT OF CHEMISTRY,
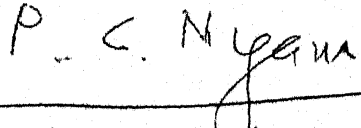INDIAN INSTITUTE OF TECHNOLOGY, KANPUR, INDIA

CERTIFICATE OF COURSE WORK

This is to certify that Mr. Periyasamy Subramanian has satisfactorily completed all the courses required for the Ph.D. degree programme. These courses include:

Chm 521   Chemical Binding

Chm 524   Physical Methods in Chemistry

Chm 541   Advanced Inorganic Chemistry I

Chm 542   Advanced Inorganic Chemistry II

Chm 626   Solid State Chemistry

Chm 800   General Seminar

Chm 801   Graduate Seminar

Chm 900   Post-Graduate Research

Mr. Periyasamy Subramanian was admitted to the candidacy of the Ph.D. degree in January, 1980 after he successfully completed the written and oral qualifying examinations.

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PERIYASAMY SUBRAMANIAN

CONTENTS

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ABBREVIATIONS

Chemicals, Ligands, Radicals, etc.

Bu	Butyl
bipy	2,2'-Bipyridyl
diars	1,2-Bis(dimethylarsino)benzene
dipic	Pyridine-2,6-dicarboxylic acid
DMF	Dimethyl formamide
DMSO	Dimethyl sulphoxide
dpam	Bis(diphenylarsino)methane
dppe	1,2-Bis(diphenylphosphino)ethane
DPPH	Diphenyl picryl hydrazyl
dtc	N,N-Dialkyldithiocarbamate
dth	2,5-Dithiohexane
en	Ethylenediamine
Me	Methyl
ox	Oxalate
Ph	Phenyl
Pr	Propyl
$P(Et)_3$	Triethylphosphine
tripos	1,1,1-Tris(diphenylphosphino)ethane
terpy	Terpyridyl
triars	1,1,1-Tris(diphenylarsino)ethane

Miscellaneous

$\overset{o}{A}$	Angstrom unit (10^{-8} cm)
BM	Bohr Magneton
ESR	Electron Spin Resonance

Abbrevations

eV	Electron Volt
FT	Fourier Transform
g	g-Values
NMR	Nuclear Magnetic Resonance
$\bar{\nu}$	Frequency (cm^{-1})
Λ_M	Molar Conductance
$\{Mo(NO)\}^n$	n denotes number of 'd' electrons

The thesis consisting the results of the investigation on "Stabilization of Lower Oxidation States of Molybdenum by Reductive Nitrosylation Using Hydroxylamine in Aqueous-Aerobic Medium" has been divided into three chapters.

In Chapter 1, a broad and general account of the chemistry of molybdenum in lower oxidation states has been given. Based on these, the scope of the present work has been outlined.

Chapter 2 describes experimental procedures and the details involved in the present work which has been divided into seven sub-headings. The first sub-heading (2.1) decribes the methods of analysis and characterization of the newly prepared compounds. Specific and selective chemical tests for the rapid identification of nitrosyl group have been outlined. Chapter 2.2 describes the preparation and properties of a series of complexes containing $\{Mo(NO)_2\}^6$ moiety, starting from reaction between molybdate(VI) and hydroxylamine. Neutral complexes having general formula $[Mo(NO)_2L_2X_2]$, $[Mo(NO)_2(L-L)X_2]$, $[Mo(NO)_2(A-A)_2]$, $[Mo(NO)_2(A-B)_2]$ (where L = neutral unidentate, L-L = neutral bidentate, A-A = homoatomic mononegative bidentate, A-B = heteroatomic dinegative bidentate ligand) and anionic complexes having general formula $[Mo(NO)_2X_4]^{2-}$ and $[Mo(NO)_2(A'-A')_2$ (where $X^- = Cl^-$, CN^- and SCN^- ; $A'-A' = C_2O_4^{2-}$) have been synthesized. Chapter 2.3 describes the preparation and properties of $Cs_2[Mo(NO)Cl_4 \cdot H_2O]$, $[Mo(NO)(o-phen)_2Cl]Cl$ and $[Mo(NO)(bipy)_2Cl]Cl$, starting from $K_4[Mo(NO)(CN)_5] \cdot 2H_2O$. Chapter 2.4 describes the preparation and properties of series

of compounds containing $\{Mo(NO)\}^4$ moiety starting from molybdate and hydroxylamine. Hexacoordinated $Cs_2[Mo(NO)Cl_5]$, heptacoordinated complex like $[Et_4N]_2[Mo(NO)(NH_2O)(NCS)_4]$ and octacoordinated $[Mo(NO)(NH_2O)(o-phen)_2(NCS)_2]$ have been synthesized. Using the same starting materials in aqueous-acetone medium, a series of N,N-dialkyldithiocarbamato complexes has been isolated. It is observed that when the alkyl group of dithiocarbamates is bulky, like n-butyl, complexes of the type $[Mo(NO)(R_2-dtc)_3]$ are formed, whereas when alkyl is a methyl group, complex of the composition $[Mo(NO)(Me_2-dtc)_2(Me_2NCSSMe)]$ is formed. Chapter 2.5 deals with the denitrosylation of $\{Mo(NO)_2\}^6$, $\{Mo(NO)\}^6$ and $\{Mo(NO)\}^4$ moieties. Electrophilic character of coordinated nitrosyl in $[Et_4N]_2[Mo(NO)_2(CN)_4]$ has also been exploited to isolate $K_4[Mo(NO)(CN)_5]$ in methanolic KCN. $K_4[Mo(NO)(CN)_5]$ has been denitrosylated to produce $[NH_4]_3[MoCl_6]$ using $SnCl_2$/hydrochloric acid. The preparation and properties of a dinuclear species $[NH_4]_3[Mo_2Cl_{11}]$ has been described by denitrosylating $\{Mo(NO)\}^4$ species using tin/hydrochloric acid. Some derivatives of this species have also been synthesized. In the sixth sub-section of this chapter, disproportionation of $\{Mo(NO)\}^4$ species into $\{Mo(NO)_2\}^6$ and MoO(IV)/MoO(V) has been demonstrated. The formation of $\{Mo(NO)_2\}^6$ from $\{Mo(NO)\}^4$ species using hydroxylamine under varied conditions are presented. The last sub-section of this chapter (2.7) deals with the bioinorgani aspect of $\{Mo(NO)\}^4$ species in the context of its role as environ mental catalyzer in the synthesis of aminoacids in prebiotic

conditions. A mechanism substantiating the role of this nitrosyl species to generate continuously HCN, starting from hydroxylamine and formaldehyde has been established.

Chapter 3 describes the physicochemical and structural investigations of the prepared compounds described in Chapter 2. The studies include IR, magnetic susceptibility, ESR, NMR, X-ray photoelectron spectroscopy and single-crystal X-ray structural determination. Structural characterization of the prepared complexes have been made in conformation with the existing theories using these techniques. Emphasis has been made to understand the nitrosylation of molybdenum with concomitant reduction using hydroxylamine, especially for the dinitrosylation step. The following stepwise reaction scheme has been proposed:

$$\{Mo(NO)(NH_2O)\}^4 \xrightarrow{-H^+} \{Mo(NO)(NHO)\}^4 \xrightarrow{-H^+} \{Mo(NO)_2\}^6$$
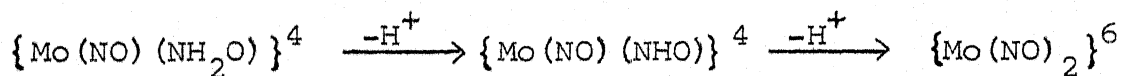
X-ray structural investigation of $[Ph_4P]_2[Mo(NO)_2(NCS)_4]$ corroborates the linear cis-dinitrosyl group attachment to molybdenum. Other structural contributions related to these species, which appeared in the literature while our work was in progress, were compared which conclusively proved the above dinitrosylation scheme.

Molybdenum, the 34th most abundant element was discovered by Hjelm in 1790 in molybdinite, MoS_2, which is its most important ore.   Besides its extensive use to improve the strength, corrosion resistance and thermal stability of ferrous alloys, chemical uses of molybdenum are limited.   But are constantly expanding because molybdenum unlike other transition metals is classified as relatively harmless to the environment[1].

Chemically molybdenum behaves similar   to its higher congener, tungsten, yet there are differences between them in various types of compounds that are all not easy to explain. Molybdenum shows resemblence to chromium only with the compounds with the π-acid ligands. As expected for the heavier elements, the higher oxidation states are most common and more stable against reduction.   Molybdenum is the only heavier transition metal that is known to be essential in the living systems.

Molybdenum can exist in different oxidation states such as -2, 0, +1, +2, +3, +4, +5 and +6. Tungsten has also similar

oxidation states and the most stable oxidation state is +6. However, the chemistry of pentavalent state of Mo has outnumbered any other oxidation states regarding the formation of innumerous compounds and the detailed studies. Compounds in tetravalent and trivalent states of molybdenum are by large less stable yet can be synthesized using solid state reactions as well as in solution.

CHEMISTRY OF LOWER OXIDATION STATES (0,I,II) OF MOLYBDENUM

Molybdenum(II)

The chemistry of Mo(II) can be divided into three distinct classes as: (i) molybdenumdichloride, (ii) compounds containing quadruply- bonded $[Mo_2]^{4+}$ and (iii) compounds with π-ligands.

(i) Molybdenumdichloride:

Mo_6Cl_{12} may be isolated by the reaction of metallic molybdenum in $COCl_2$ at 630° [2]. This is a cluster compound consisting of an octahedran of the metal atom with the bridging chlorides on each triangular face to give a cationic cluster unit $[Mo_6Cl_8]^{4+}$. It is possible to obtain compounds in which a wide variety of ligands may occupy the outer position like $[Mo_6Cl_8]Br_4$. The octahedral unit is relatively inert to redox reactions despite the low formal oxidation number.

Perrin and coworkers [3] obtained compounds of composition $Mo_6Cl_{10}S$ (or Se/Te analogue) by sealed tube reactions of $MoCl_5$,

Mo and sulphur or selenium or tellurium. Mixed compounds like $Mo_6S_6Br_2$ and $Mo_6S_6I_2$ can also be synthesized which are super-conductors below 14°K [4].

(ii) Compounds containing quadrupoly-bonded $[Mo_2]^{4+}$

The first compound of this exceptional class was first synthesized by refluxing $Mo(CO)_6$ in glacial acetic acid acetic anhydride to give $[Mo_2(OAc)_4]$ [5]. This molecule is shown by Lawton and Mason [6] to have a quadruply-bridged structure analogous to $Cu(OAc)_2 \cdot 2H_2O$, but containing an extremely short Mo-Mo bond. Cotton and coworkers [7] have shown that this compound reacts at 0°C with concentrated hydrochloric acid to give $[Mo_2Cl_8]^{4-}$ which can be trapped by several cations. These compounds are isoelectronic to $[Re_2Cl_8]^{2-}$ ion. Major chemistry of this class of compounds has been studied by Cotton's group and some important reactions of this two key species are summarised in Scheme I:

Bowen and Taube [8a,8b] showed the existence of $[Mo_2]^{4+}$ (aq.) ions by dissolving $[Mo_2Cl_8]^{4-}$ in CF_3SO_3H. One-electron oxidation product of $[Mo_2(SO_4)_4]^{4-}$ can be crystallized as $K_3[Mo_2(SO_4)_4] \cdot 2H_2O$. The structures of these two units are remarkably similar, with the later having somewhat longer Mo-Mo distance. The oxidised anion gives e.s.r. signal and the magnetic moment is 1.65 B.M. In the oxidised state, each Mo may be thought to contain an oxidation state of +2,5 which can be reduced to the

4

$[Mo_2(aq.)]$

$[Mo(CNR)_7]^{2+}$

$[Mo_2(SO_4)_4]^{4-}$

$[Mo_2(SO_4)_4]^{3-}$

$[Mo_2(HPO_4)_4]^{3-}$

$[Mo_2Cl_8]^{4-}$

$[Mo_2Cl_8H]^{3-}$

$[Mo_2(OAc)_2(acac)_2]$

$[Mo_2(OAc)_4]$

$[Mo_2(XAN)_4X_2]$

$[MoOX_4(H_2O)]^-$

CF_3SO_3H (aq.)

H_2SO_4 (aq.)

$[H_2SO_4]$ O_2

$[H_3PO_4]$ O_2

HCl $50°$

HCl (aq.)

NRC

acac

S_2COR^-

X_2

HX (aq.) O_2
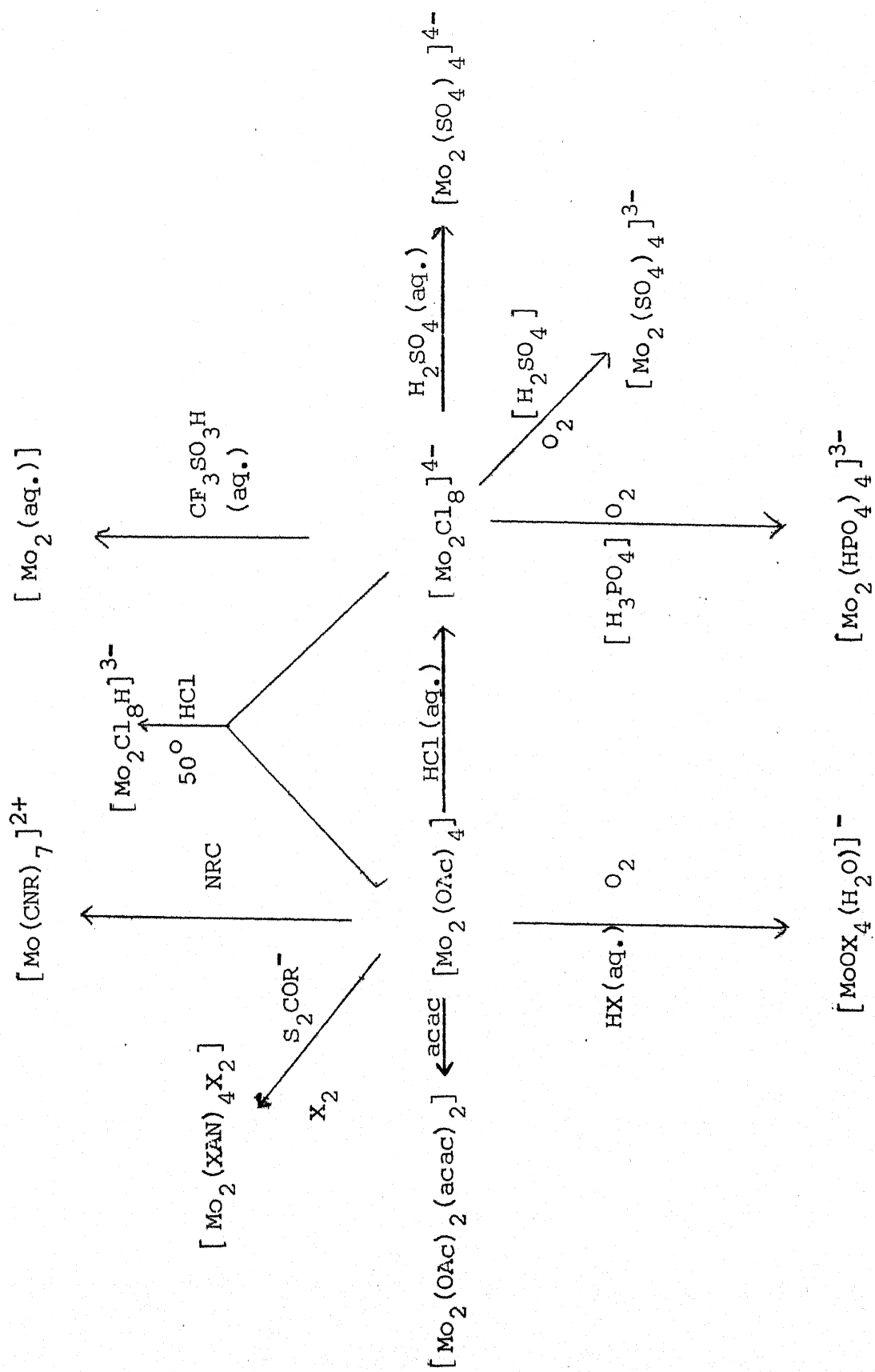
SCHEME 1.1. Some Important Reactions Involving Mo-Mo Quadruple Bonds

dimeric $[Mo_2]^{4+}$ species by Jones reductor [9]. However, the corresponding chloro-complex on oxidation gives $[Mo_2Cl_8H]^{3-}$ [10]. Heteronuclear metal-metal bonding can also be achieved like in $[CrMo(OAc)_4]$ by adding $Mo(CO)_6$ in glacial acetic acid and dichloromethane to refluxing $Cr(OAc)_2 \cdot 2H_2O$ in glacial acetic acid - acetic anhydride [11].

Green and Silverthrone had prepared the complex $[(C_6H_6)(C_3H_5)MoCl]_2$ [12] which is a dinuclear Mo-Mo compound having little resemblance to the complexes of the $[Mo_2]^{4+}$ species. This diamagnetic compound has two bridging chlorides, one π bound benzene and a π-bound allyl per molybdenum and the Mo-Mo distance is sufficiently apart.

(iii) Compounds with π-ligand:

The complexes in this class are mostly organometallic in nature and the majority of them have been synthesized starting from $Mo(CO)_6$ by oxidation and substitution reactions. There is to date no aqueous chemistry of monomeric Mo(II).

The first set of this class of compounds were reported by Lewis [13] and Nyholm [14-16], Stiddard [17], Wilkinson [18] and their coworkers. Representative reactions to illustrate these syntheses are described in reactions 1 to 3.

$$[Mo(CO)_4(bipy)] + Br_2 \longrightarrow [Mo(CO)_2(bipy)Br_2] + 2\ CO \qquad ..(1)$$

$$[Mo(CO)_4(dth)] + I_2 \longrightarrow [Mo(CO)_2(dth)I_2] + 2\ CO \qquad ..(2)$$

$$[Mo(CO)_2(diars)_2] + 2\ Br_2 \longrightarrow [Mo(CO)_2(diars)_2Br]Br_3 \qquad ..(3)$$
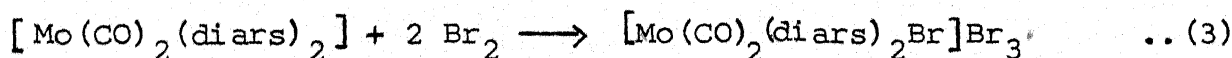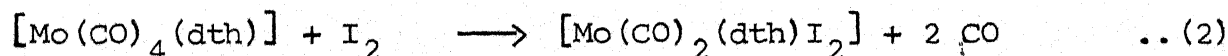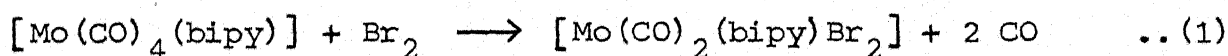
Substituted derivatives of $Mo(CO)_3$ with neutral ligands like mono-, bi-, tri- and tetradentate phosphines, as well as mono- and bidentate arsines have been oxidised by halogens to give a series of mixed ligand Mo(II) complexes. Some representative complexes using above mentioned synthetic route include $[Mo(PEt_3)_2(CO)_3Cl_2]$ [19], $[Mo(CO)_2(phen)_2I]I_3$ [20], $[Mo(CO)_3(dppe)Br_2]$[13], $[Mo(CO)_2(triphos)I_2]$ [21], $[Mo(CO)_2(triars)I_2]$ [15].

Colton and coworkers [22-29] used an alternative technique of first oxidising $Mo(CO)_6$ with halogens and then adding the neutral ligands as

$$Mo(CO)_6 + X_2 \xrightarrow[(X = Cl, \ Br, \ I)]{} [Mo(CO)_4X_2] + 2\ CO \qquad ..(4)$$

$$[Mo(CO)_4Cl_2] + 2\ PPh_3 \longrightarrow [Mo(PPh_3)_2(CO)_2Cl_2] + 2\ CO \quad ..(5)$$

$$[Mo(CO)_4Cl_2] + 2\ NaR_2dtc \longrightarrow [Mo(CO)_3(R_2dtc)_2] +$$
$$2\ NaCl + CO \quad ..(6)$$

$$[Mo(CO)_4Br_2] + 2\ dpam \longrightarrow [Mo(Br)_2(CO)_2(dpam)_2] + 2\ CO \ ..(7)$$
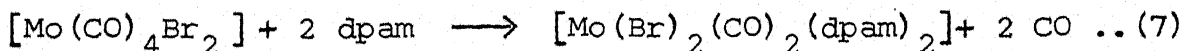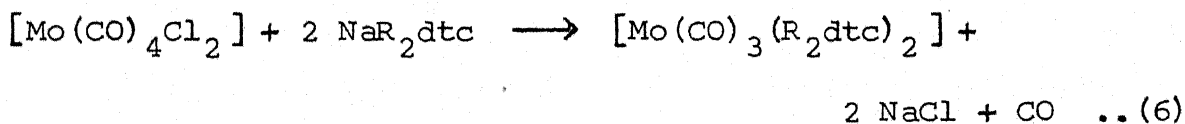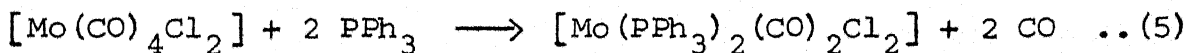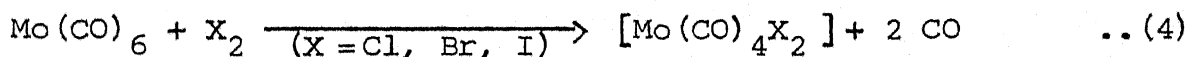
Most of the complexes are having a seven coordinate geometry, but in the case of $[Mo(CO)_2Br_2(dpam)_2]$, the stereochemistry suggests an 8-coordination. Actually one of the bidentate ligands is acting in a monodentate mode [30].

An interesting reaction is observed with many of the yellow seven coordinate complexes of this type containing phosphine type of neutral ligands. Thus the tricarbonyl derivatives like $[Mo(PR_3)_2(CO)_3X_2]$ (X = Cl, Br) readily loose one mole of CO to form diamagnetic blue complexes $[Mo(PR_3)_2(CO)_2X_2]$ [24,26,19]. The complex $[Mo(PPh_3)(CO)_2Br_2]$ has been shown to contain an unusual non-octahedral 6-coordinate arrangement containing Mo(II) ions [31]. The corresponding dithiocarbamate compound also has the interesting property which leads to some unusual reactions as noted below:

$$[Mo(CO)_3(R_2dtc)_2] \rightleftharpoons [Mo(CO)_2(R_2dtc)_2] + CO \qquad [24,27] \quad ..(8)$$

$$[Mo(CO)_2(dtc)_2] + CH\equiv CH \longrightarrow [Mo(CO)(dtc)_2(C_2H_2)] + CO \quad [32] \quad ..(9)$$
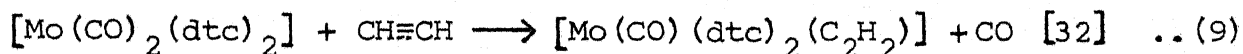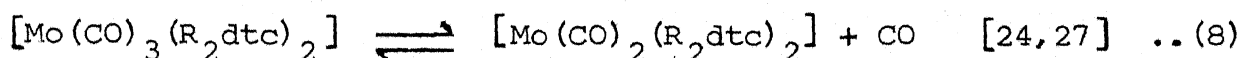
The reaction (9) does not go with ethylene. The acetylenic protons in the compound occur at 12.3 ppm down-field of TMS and no C=C stretch is observed in the infrared which is presumed by the use of π-levels of CH$\equiv$CH as donors to satisfy the 18-electron rule. Treatment of this compound with acid produces ethylene. It is interesting to note that the 6-coordinate Mo(II) complex coordinately binds unsaturated CH$\equiv$CH and not $CH_2=CH_2$ [32] and with CO gives seven coordinated species. All these reactions have relevance to the nitrogenase.

$[(C_5H_5)_2Mo(CO)]$ upon irradiation in the presence of CH$\equiv$CH forms $[(C_5H_5)_2Mo(C_2H_2)]$ [33]. Hence the acetylenic proton

appears at 7.8 ppm downfield from the TMS and $\nu_{C=C}$ at 1616 cm^{-1}.
In this case $(C_5H_5)Mo$ fragment has a 16-electron core and the
CH≡CH uses only one set of π-orbitals for bonding to acquire an
18-electron configuration. The contrast between binding of
CH≡CH with 14-and 16-electron core is noteworthy.

Anionic salts like $[Mo(CO)_4X_3]^-$ can also be synthesized
[28,34]. $[Mo(RNC)_7]X_2$ has been prepared from $Mo(CO)_6$ and RNC
or by reaction of $Ag_4[Mo(CN)_8]$ and tertiarybutyl-iodide in $CHCl_3$
containing AgCN [35]. $[Mo(RNC)_5 X_2]$ can be prepared from $Mo(CO)_4X_2$
and RNC [36], whereas reaction of $Ag_4[Mo(CN)_8]$ and tertiary-
butyl-iodide gives $[Mo(RNC)_6I]I$ [37]. The $[Mo(NO)(R_2-dtc)_3]$
which can be regarded as Mo(II) complexes have been prepared
by the following reaction [38]:

$$Mo(CO)_6 \xrightarrow[-78^\circ C]{Cl_2} [Mo(CO)_4Cl_2] \xrightarrow{NOCl}$$

$$[Mo(NO)Cl_3] \xrightarrow{Nadtc} [Mo(NO)(dtc)_3] \quad\quad ..(10)$$
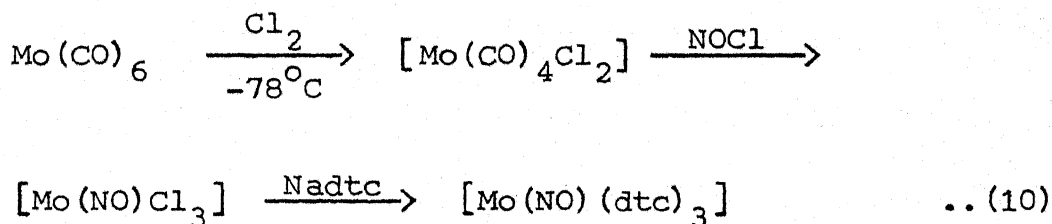
Here Mo-N-O is linear and the compound has a seven-coordinate
structure of pentagonal bipyramid [39,40].

Anaerobic reaction of acidic Mo(III) halides solution with
diarsine in water and/or alcohol leads to the isolation of an
interesting class of 6-coordinate complexes $[MoX_2(diars)_2]$ (X = Cl,
Br, I) [41]. The compounds are paramagnetic corresponding to
2 unpaired electrons.

Other coordinate complexes $[Mo(diars)(CO)_2I_2][42]$, $[Mo(Py)_2(CO)_2X_2]$ (X = Cl, Br) are also found to be paramagnetic [43]. Sometimes dimeric complexes like $[MoX_2(CO)_2((Me_2Ph)P)_2]_2$ have also been reported.

Nitrosylmolybdenum compounds can also be synthesized by the cleavage of Mo–Mo multiple bonds using NO. The first example of this type of reactions came through the work of King and coworkers [44]. Recently, Cotton and coworkers [45] extended this reactivity even in electronically unsaturated Mo–Mo triple bond containing compounds with NO. The reactions are:

$$[(Me_5C_5)_2Mo_2(CO)_4] + 2\ NO \longrightarrow 2\ [(Me_5C_5)Mo(CO)_2NO] \qquad .. \ (11)$$

$$[Mo_2(OR)_6] + 2\ NO \longrightarrow [Mo_2(OR)_6(NO)_2] \qquad .. \ (12)$$
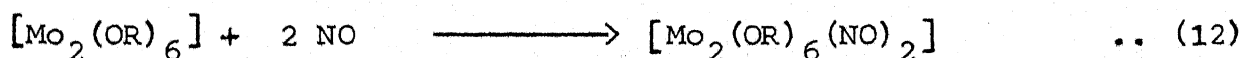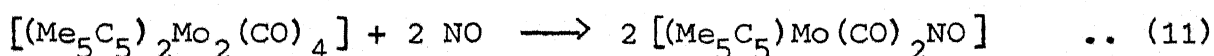
(R = Me_3C; Me_2CH; Me_3CCH_2).

Molybdenum(I)

The evidence of this oxidation state of molybdenum came through an e.s.r. study of the oxidation of $K_4[Mo(NO)(CN)_5]$ [46]. Only recently, this compound has been characterised in the form of $(PPh_4)_3[Mo(NO)(CN)_5].2H_2O$ [47]. An unusual compound $Cs_2[Mo(NO)Cl_4.H_2O]$ has been isolated in concentrated hydrochloric acid medium [48]. As expected, the magnetic moment corresponds to the spin only value for one unpaired electron.

The proposed structure has recently been confirmed by X-ray crystallography [49]. The complex $[Mo(N_2)_2(dppe)_2]I_3$ was isolated by oxidising $[Mo(N_2)_2(dppe)_2]$ with iodine in methanol [50]. The magnetic moment, 1.97 B.M. is unusual as it is greater than the spin-only value and stands in contrast to that of $Cs_2[MoNOCl_4.H_2O]$ and to that found for $[Mo(CO)_2(dppe)_2 I_3]$ However, $(PPh_4)_3[MoNO(CN)_5].2H_2O$ also has a higher magnetic moment, 1.93 B.M. [47]. Trans-$[MoCl(N_2)(dppe)_2]$ and the bromo-analogue are also reported [51,52]. Complexes using benzene and cyclopentadiene like $(C_6H_6)_2Mo^+$, $[(\eta^5-C_5H_5)MoC_6H_6]$ are also known [53].

Molybdenum(0)

Since the inception of carbonyl chemistry, this formal oxidation state of molybdenum is well known in $Mo(CO)_6$, and a host of its substituted derivatives having the general formula $[LMo(CO)_5]$, $[L_2Mo(CO)_4]$, $[L_3Mo(CO)_3]$ (where L = donor ligands). When $Mo(CO)_6$ is allowed to react with KI in diglyme, the anionic complex $[K(diglyme)_3][Mo(CO)_5I]$ is formed [54]. Other ligands which in general stabilize this oxidation state are isoelectronic with carbon monoxide and they are NO^+ and N_2. The dinitrogen complex is very interesting in the sense that the identification of trends of dinitrogen binding and activation may help to focus on the nature of the active site in the enzyme nitrogenase. Trans-$[Mo(N_2)_2(dppe)_2]$which is by far the most thoroughly studied molybdenum dinitrogen complex. Several

methods of preparation of this compound have been reported and

ranging from a five day waiting period prior to isolation of the

product in 13% yield to 3 hr reaction with 88% yield [51,55-58].

The most successful reaction scheme, followed by Chatt and

coworkers [59,60], is as follows:

$$MoCl_5 \xrightarrow[\text{reflux}]{\text{EtCN}} [MoCl_4(EtCN)_2] \xrightarrow[\text{CH}_2\text{Cl}_2/\text{THF}]{\text{Zn}}$$

$$[MoCl_3(THF)_3] \xrightarrow[\text{(dppe)/N}_2]{\text{Na(Hg)}} \text{trans-}[Mo(N_2)_2(dppe)_2]$$

.. (13)
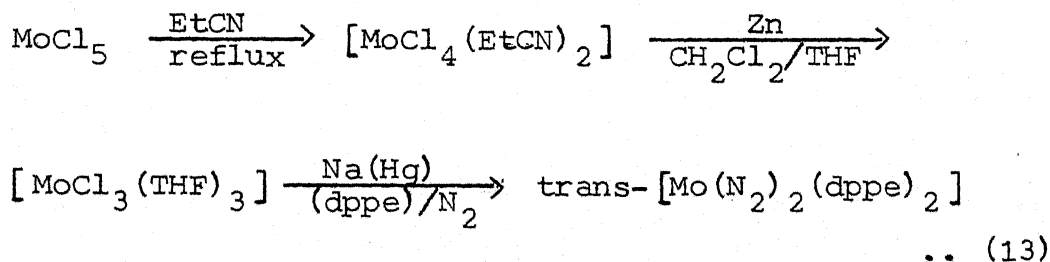
Complexes analogous to this compound have been formed

with other bidentate phosphine and arsine ligands. With mono-

dentate phosphines, besides trans-dinitrogen arrangement,

cis- arrangement has also been reported [58, 59, 61].

Trans-$[Mo(N_2)_2(dppe)_2]$ reacts reversibly with ethylene [62] at

high temperature to give $[Mo(C_2H_4)(dppe)_2]$. This reaction is

unusual as it involves an 18-electron octahedral complex react-

ing with ethylene to produce an apparently five-coordinate 16-

electron species. As iron and molybdenum both are present in

nitrogenase, the following reactions demonstrate some of the

complexities in the relationship between N_2 and H_2 binding

sites in the enzyme [61]:

$$\text{trans-}[Mo(N_2)_2(dppe)_2] + FeH_4P_3 \longrightarrow [MoH_2(dppe)_2] + [FeH_2N_2P_3] + N_2$$

.. (14)

trans-$[Mo(N_2)_2(dppe)_2]$ + $2FeH_4P_3$ ⟶ $MoH_2(dppe)$ + $2FeH_2N_2P_3$+N_2

$$...(15)$$
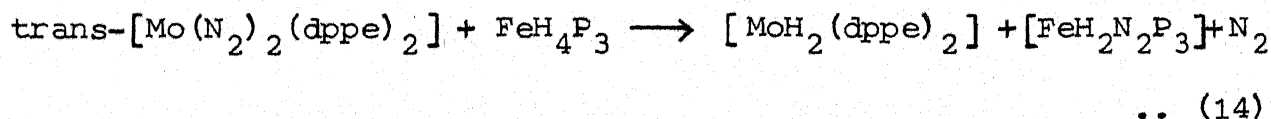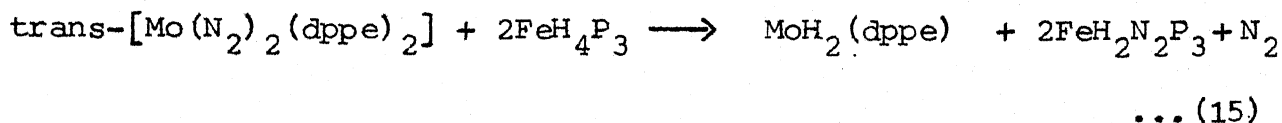
Dinitrogen compounds with bidentate phosphine ligands behave differently from the compounds containing monodentate phosphines under protonic acids,

$[Mo(N_2)_2(dppe)_2] \xrightarrow[\text{methanol}]{H_2SO_4} [Mo(dppe)_2(HSO_4)(NNH_2)]^+ + N_2$ ..(16)

$[Mo(N_2)_2(PMePh_2)_4] \xrightarrow[\text{methanol}]{H_2SO_4} NH_3 + Mo(VI)$ ..(17)
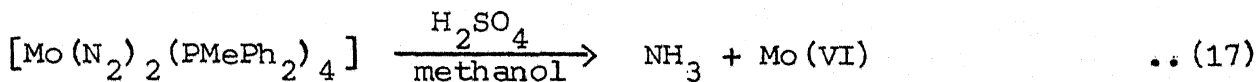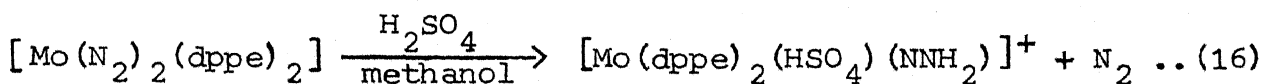
Thus the formation of ammonia as proposed by Chatt and coworkers [60,63] can be schematically shown as

M–N≡N $\xrightarrow{H^+}$ M–N=NH $\xrightarrow{H^+}$ M–N–NH$_2$ $\xrightarrow{H^+}$ M–NH–NH$_2$

$\downarrow H^+$

M(VI) + NH$_3$ $\xleftarrow{H^+}$ M–NH$_2$ $\xleftarrow{H^+}$ M=NH + NH$_3$ ..(18)
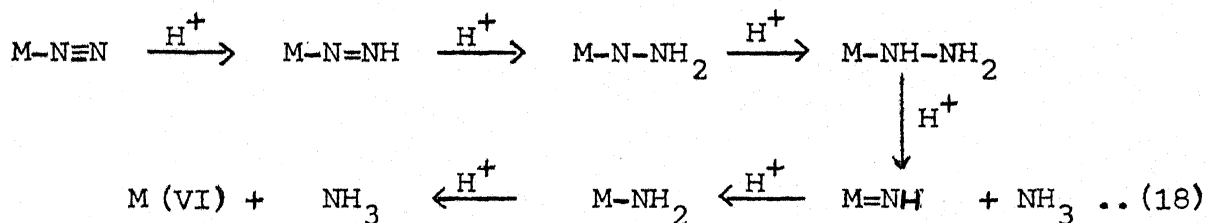
Amongst nitrosyl compounds, the 'Heide-Hofmann' cyanide is the oldest compound known which took a long way to be established as $K_4[Mo(NO)(CN)_5]$ as proposed by Hieber and coworkers [46,64,65]. From the synthetic point of view, the 'Heide-Hofmann' method has been exploited to get many organonitrosyl compounds. The interest lies in this methodology that it is the only compound of zerovalent molybdenum which can be isolated in aqueous medium.

Using NOCl as the nitrosylating reagent, Cotton and Johnson [66] used the following route to synthesize dinitrosylmolybdenum derivatives:

$$Mo(CO)_6 + 2\ NOCl \longrightarrow [Mo(NO)_2Cl_2]_n + 6\ CO \qquad ..(19)$$
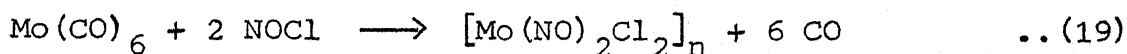
In the same year an alternative synthetic route for this type of compounds appeared involving bubbling of NO and HCl in ethanolic solution of $Mo(CO)_6$ [67a]. Colton and coworkers synthesized complexes containing dinitrosylmolybdenum moiety using the following scheme [67b]:

$$Mo(CO)_6 \xrightarrow{X_2} [Mo(CO)_4X_2] \xrightarrow{PPh_3}$$

$$[Mo(CO)_3X_2(PPh_3)_2] \xrightarrow{NO} [Mo(NO)_2X_2(PPh_3)_2] \qquad ..(20)$$
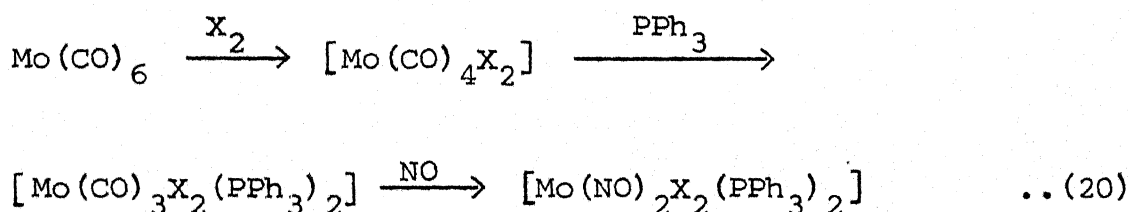
Interestingly, all the above methods involve $Mo(CO)_6$ as the starting material. Contrary to these, a reductive nitrosylation by passing NO through the solution of $MoCl_5$ in CH_2Cl_2 has been achieved to get complexes containing dinitrosylmolybdenum moiety as the final product. The intermediate mononitrosyl derivatives containing formal bivalent molybdenum can also be made [68].

There is a recent report that hexavalent molybdenum in hydrochloric acid on reduction with tin and reacting the

resultant product with NO for a long period in air-free atmosphere
generates dinitrosylmolybdenum moiety which can be reacted with
bipy- or o-phen to give $(LH_2)[Mo(NO)_2Cl_4]$ (where L = bipy,
o-phen) and with CsCl to give $Cs_2[Mo(NO)_2Cl_4]$ [69].

Compounds containing Mo-Mo multiple bonds on reaction with
NO can afford dinitrosylmolybdenum derivatives. The reaction is
parallel to that observed for the cleavage of Mo-Mo triple bond
to get mononitrosyl-molybdenum derivatives (vide supra). Interest-
ingly dinitrosyl derivatives are formed when Mo-Mo quadruply-
bonded compounds are cleaved with NO [70,71]. The preparative
chemistry of nitrosylmetal complexes is complex and varied.
As for synthesis of carbonyl compounds, the high temperature
and high pressure reactions are employed whereas nitric-monoxide
can not be used as a nitrosylating agent in this fashion due to
its oxidising property and also its thermodynamic instability
as

$$3 \text{ NO} \longrightarrow N_2O + NO_2 \qquad \Delta H = -37.2 \text{ kcal mol}^{-1} \qquad ..(21)$$

$$NO \longrightarrow \tfrac{1}{2} N_2 + \tfrac{1}{2} O_2 \qquad \Delta H = -21.6 \text{ kcal mol}^{-1} \qquad ..(22)$$
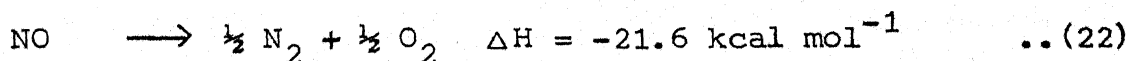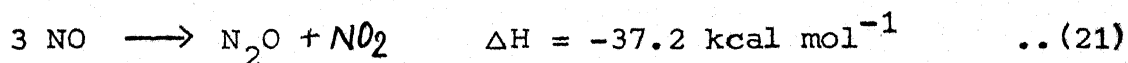
Due to these reasons, the new approaches in synthesizing
nitrosyl complexes came out. For metal complexes with NO, a
brief discussion concerning electron counting rules appropriate
to the nitrosyl group is required. This has a direct consequence
on assigning the formal oxidation states of transition metal ions

coordinated with NO. In general, for a metal ion, M^{n+} which bonded with NO, may acquire an electronic configuration either $\{MNO\}^{n+}$ or $\{MNO\}^{n-1}$ in the light of coordinated NO as NO^+ and NO^- respectively. This is due to the low ionization potential of NO (9.23 eV) to give NO^+. It is assumed that an electron transfer first takes place from NO to the metal to form NO^+ which proceeds to the coordination of the nitrosonium ion through the nitrogen lone pair. This sigma donation is re-inforced by the π-back donation from metal to π^* orbital of NO^+. In this scheme the coordination of NO thus takes place in the form of 3-electron donation. The other isoelectronic ligands (N_2, CO) compared to NO^+ are formally 2-electron donors. From the molecular orbital description it is apparent that the π-bonding description leads to the linear mode of coordination. However, the wide variation of NO for this type of coordination is a bit misleading which can be best rationalised from the valence bond picture:

$$
\begin{array}{ccc}
\ddot{O} & & :O: \\
||| & & || \\
N & \longleftrightarrow & N \quad \longleftarrow \ sp \\
| & & || \\
M & & M
\end{array}
$$
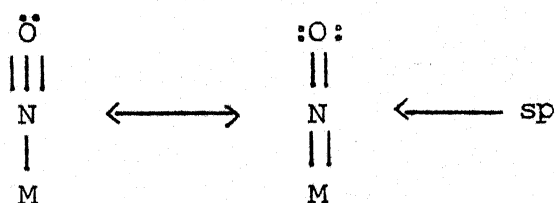
Linear mode of bonding

In the other extreme type of bonding in metal-nitrosyl complexes the metal, nitrogen and oxygen atoms are not colinear.

Here the NO^+ is believed to behave as a Lewis acid contrary to the metal ion resulting in the acceptance of an electron pair from the metal (base) to NO^+. This means NO can be treated here formally as (one electron donor and the resulting charge on NO should be NO^-. The valence bond picture suggests two cononical forms for this type of attachment as:
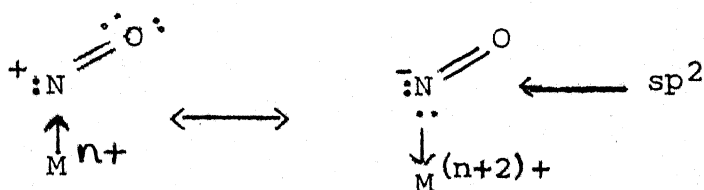
The terminal nitrogen bonding in nitrosyls thus can have these two extreme formalism and the real picture lies somewhere in between these two extremes. Thus facile introduction of NO in complexes containing either a-17 or 15-electron configuration is possible so that NO can supply one or three electrons to achieve inert gas configuration:

$$Cr(NR_2)_3 \longrightarrow [Cr(NO)(NR_2)_3] \quad [72] \qquad ..(23)$$

$$[CoCl_2L_2] \longrightarrow [Co(NO)Cl_2L_2] \quad [73] \qquad ..(24)$$
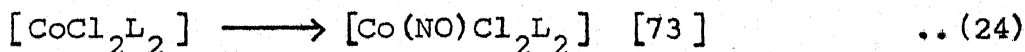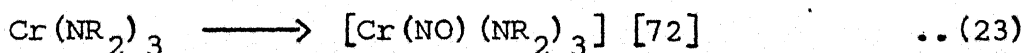
However, introduction of the NO group sometime may not lead to an inert gas configuration, like a 14-electron species can be converted into a 15-electron species:

$$[Fe(chel)_2] \longrightarrow [Fe(NO)(chel)_2] \quad [74] \qquad ..(25)$$
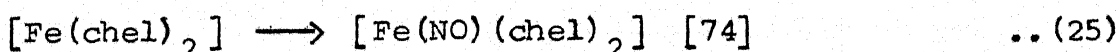
The demand to achieve an 18-electron configuration can be met by substitution, replacement of ligands equivalent to 3 electrons or even reductive nitrosylation.   Some representative examples are

$$Cr(CO)_6 \xrightarrow[NO]{h\nu} Cr(NO)_4 \qquad [75,76] \qquad ..(26)$$

$$[Ru(S_2CNEt_2)_3] \longrightarrow [Ru(NO)(S_2CNEt_2)_3] \; [77] \qquad ..(27)$$

$$[Mn(CO)_5I] \longrightarrow [Mn(NO)_3(CO)] \qquad [78] \qquad ..(28)$$

$$MoCl_5 + NO \longrightarrow [Mo(NO)_2Cl_2]_n + 3 \; NOCl \; [68] \qquad ..(29)$$
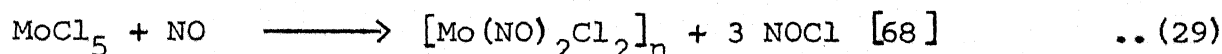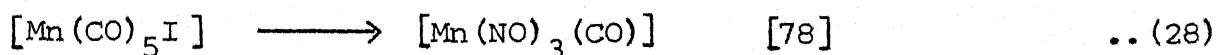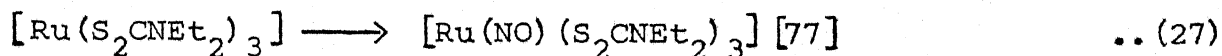
Complexities arise when the precursor metal complex lacks an even number of electrons from the inert gas configuration as in the case of metal clusters:

$$[Mn_2(CO)_8L_2] \longrightarrow [Mn(NO)(CO)_4] + [Mn(NO)(CO)_3L] + L \; [78,79] ..(30)$$

$$[Co(dppe)_2]^+ \longrightarrow [Co(NO)_2(dppe)]^+ \quad [80] \qquad ..(31)$$
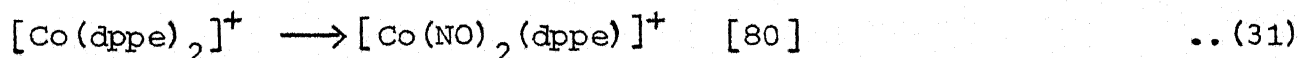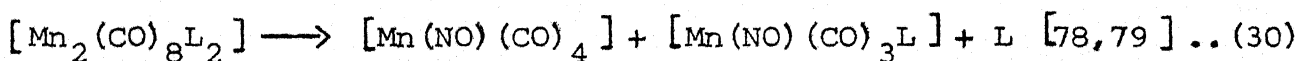
Interestingly, besides the cleavage of M-M single or multiple bonds by nitrosylation, these bonds can even be introduced as;

$$[CpFe(CO)_2]_2 \longrightarrow [CpFe(NO)]_2 \quad [81] \qquad ..(32)$$

$$[H_3IrL_2] \longrightarrow [Ir(NO)_2L]_2 \quad [82] \qquad ..(33)$$
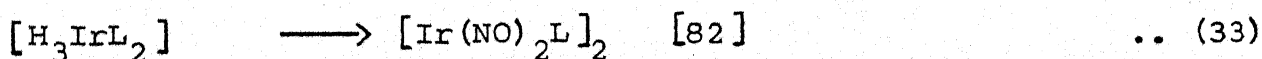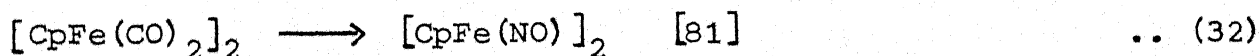
Nitrosyl complexes can also be prepared using salts of the NO^+X^- as the source of NO^+. However, due to the hydrolytic sensitivity of these salts, the reactions are to be carried out in passive solvents.

Essentially, use of nitrosyl salts can be taken as addition or substitution reactions. Sometimes oxidative addition may occur to coordinately unsaturated substrates as:

$$[Ru(NO)ClL_2] \longrightarrow [Ru(NO)_2ClL_2]^+ \qquad [83] \qquad ..(34)$$

$$[Cr(CO)_4(dppe)] \longrightarrow [Cr(NO)_2(CH_3CN)_4]^{2+} [84,85] \qquad ..(35)$$

$$[RuCl_2L_4] \longrightarrow [Ru(NO)Cl_3L_2] \qquad [86] \qquad ..(36)$$
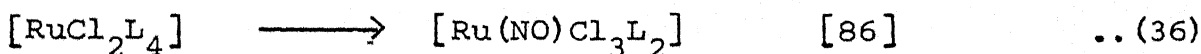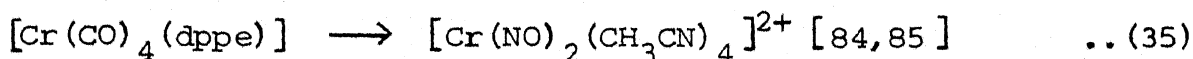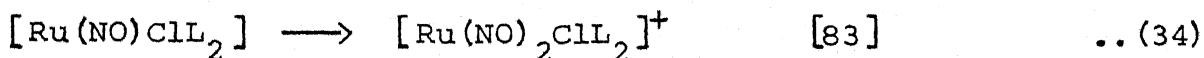
The oxidative addition is believed to be due to the existence of the following equilibrium:

$$2 \, NOX \rightleftharpoons 2 \, NO + X_2 \qquad\qquad ..(37)$$

N-Nitrosoamides react with metal hydrides to produce metal nitrosyls. This reaction replaces a hydrogen atom along with the extrusion of a 2-electron donor ligand resulting in a linear nitrosyl complex. For example,

$$[HMn(CO)_5] \longrightarrow [Mn(CO)_4(NO)] + CO \; [87] \qquad ..(38)$$
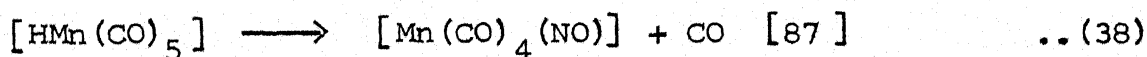
Simple nitrosyl transfer from a coordinated nitrosyl complex with the other metal complex is known. A representative example

$$[Co(NO)(DMG)_2] + [RuL_3Cl_2] \longrightarrow [Ru(NO)ClL_2] + [CoCl(DMG)_2L] \, [88]$$

.. (39)
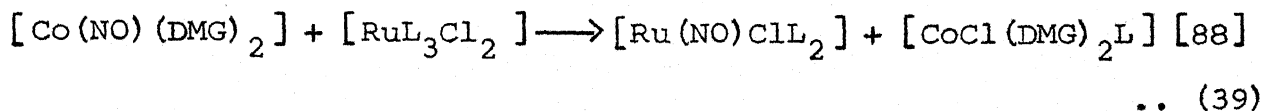
NO^+ in protic solvents is linked by the following equilibrium to alkyl nitrites

$$RONO + H^+ \rightleftharpoons NO^+ + ROH \qquad \qquad .. (40)$$
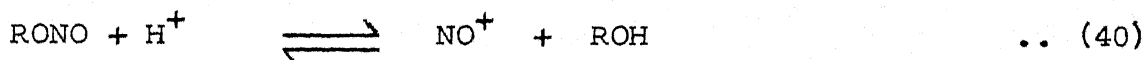
Thus $[Fe(NO)(CO)_2(PPh_3)_2]^+$ can be generated from $[Fe(CO)_3(PPh_3)_2]$ in a solution of isopentylnitrite and HPF_6 in benzene/methanol[89]. The use of NO_2^-/H^+ to form nitrosyl complex is long known and one of the most complicated reactions involved using this reagent in the preparation of Roussian's black salt [90] is

$$52 \, FeSO_4 \cdot 7H_2O + 42 \, NaNO_2 + 34 \, (NH_4)_2S + 4 \, H_2O \longrightarrow$$

$$6 \, (NH_4)[Fe_4S_3(NO)_7] + 28 \, Fe(OH)_3 + 16 \, S + 21 \, Na_2SO_4 + 31 \, (NH_4)_2SO_4$$

..(41)
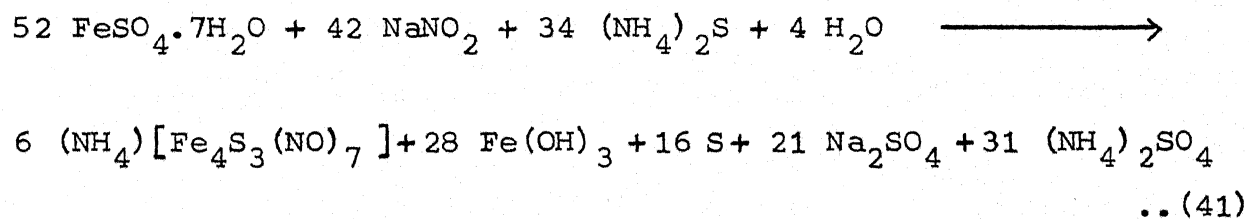
The use of nitric acid as nitrosylating reagent is the first one used by Playfair in 1849 for the synthesis of $Na_2[Fe(NO)(CN)_5]$ from $Na_4[Fe(CN)_6]$[91].

As the present work deals with the nitrosylation of molyb-
denum using hydroxylamine as a reductive nitrosylating reagent,
it would not be out of place to mention in detail about this
nitrosylating reagent.

Hieber and coworkers first exploited the use of hydroxyl-
amine as nitrosylating reagent [92,93]. Tracing back the obser-
vation made by Heide and Hofmann [64], the formulation of this
compound according to them is $K_4[Mo(NO)(CN)_5].2H_2O$. However,
Griffith, Lewis and Wilkinson [94] proposed an alternative octa-
coordination structure for this compound: $K_4[Mo(NO)(CN)_5(OH)_2]$.
X-ray studies confirm the hexa-coordinated structure without any
water of crystallization $K_4[Mo(NO)(CN)_5]$ [65]. Wilkinson and
coworkers did an extensive work using hydroxylamine in strongly
alkaline/cyanide medium with other oxometallate anions. Thus
with CrO_4^{2-}, the green complex $K_3[Cr(NO)(CN)_5].H_2O$ was isolated[94].
Similarly using the same procedure with VO_3^-, the orange complex
$K_5[V(NO)(CN)_5].H_2O$ has been isolated [95] which is structurally
characterized as $K_3[V(NO)(CN)_5].2H_2O$ [96]. Interestingly, using
the slightly different procedure that is with VO_3^- and $NH_2OH/KOH/$
KCN/, passing of H_2S leads to the isolation of an yellow complex
$K_4[V(NO)(CN)_6].H_2O$ [97]. The hydroxylamine method can also be
applied to some cyano complex as the precursor   to be
nitrosylated. Thus $K_3[Mn(CN)_6]$ can be converted into purple
$K_3[Mn(NO)(CN)_5].2H_2O$ by this method [98]. Similarly purple
$K_2[Ni(NO)(CN)_3]$ can be synthesized by the reaction of hydroxyl-
amine with $K_2[Ni(CN)_4]$ [99]. Besides cyanide as a coligand,

nitrosyl complexes can be generated by alkaline hydroxylamine in another way as

$$[Co(CNR)_5X] + 2 NH_2OH \longrightarrow$$

$$[Co(NO)(CNR)_3] + 2 RNC + H_2O + NH_4X \quad [100] \quad ..(42)$$
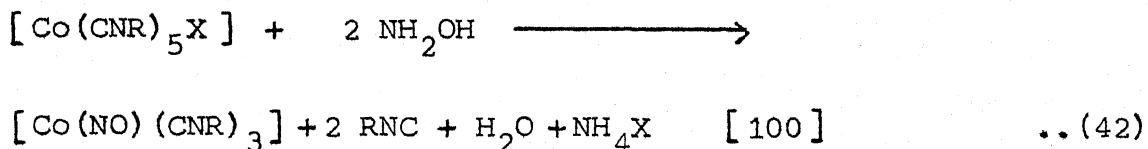
All the above mentioned compounds, which are synthesized by the hydroxylamine method, require strong alkaline medium. Hieber and coworkers proposed the demand for strong alkali in the following way [64]:

$$2 NH_2OH \longrightarrow NOH + NH_3 + H_2O \quad\quad ..(43)$$

$$NOH + OH^- \longrightarrow NO^- + H_2O \quad\quad ..(44)$$
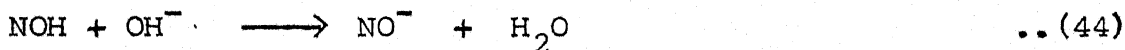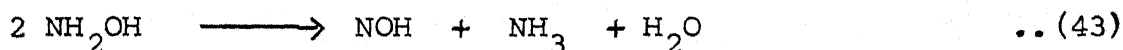
The formation of 'NOH' requires strong alkali to deprotonate to generate NO^- which can act as a reductive nitrosylating source. The decomposition of hydroxylamine in alkali is very complicated whereby a lot of species like N_2, N_2O, $N_2O_2^{2-}$, NO_2^- can be formed. Traces of impurities like some metal ions can catalytically decompose hydroxylamine to N_2 and NH_3. However, the formation of $N_2O_2^{2-}$ may be thought by the dimerization of NO^-. A kinetic study of the reaction of hydroxylamine with $[Ni(CN)_4]^{2-}$ in alkaline medium suggests that in the presence of oxygen, the reaction is

$$[Ni(CN)_4]^{2-} + NH_2OH + \tfrac{1}{2}O_2 + OH^- \longrightarrow$$

$$[Ni(NO)(CN)_3]^{2-} + CN^- + 2H_2O \qquad [101] \qquad ..(45)$$
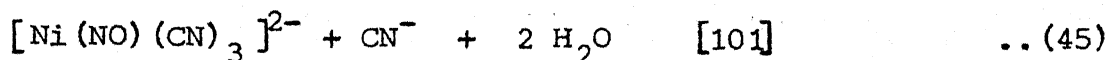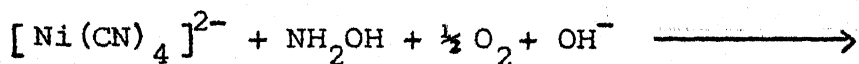
The explanation provided for the reaction is that no ammonia is produced that involves a pre-equilibrium in which hydroxyl-amine replaces CN^-. Deprotonation of coordinated NH_2OH followed by oxidation of the resultant $[Ni(NO)(CN)_3]^{4-}$ by oxygen completes the reaction. In the absence of oxygen, the reaction is very slow and kinetically less tractable where the mechanism may be as follows:

$$[Ni(CN)_4]^{2-} + NH_2OH \longrightarrow [Ni(NH_2OH)(CN)_3]^- + CN^- \qquad ..(46)$$

$$[Ni(NH_2OH)(CN)_3]^- + NH_2OH + OH^- \longrightarrow$$

$$[Ni(NO)(CN)_3]^{2-} + NH_3 + 2H_2O \qquad ..(47)$$
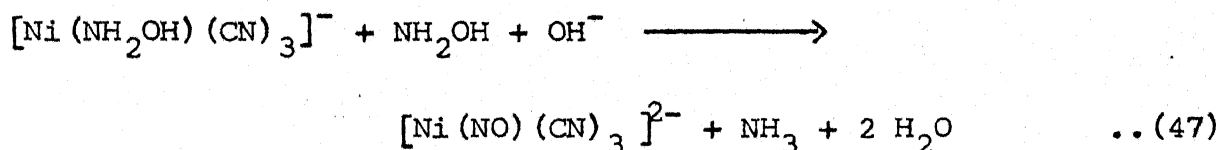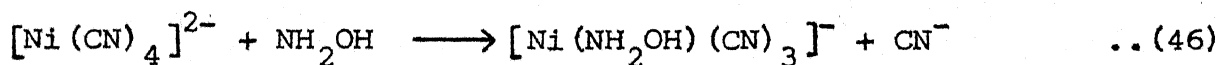
The stoichiometry regarding the ammonia produced per mole of $[Ni(NO)(CN)_3]^{2-}$ formed and NH_2OH used can not be set properly because of the side reactions like,

$$[Ni(NO)(CN)_3]^{2-} + NH_2OH + CN^- \longrightarrow$$

$$[Ni(CN)_4]^{2-} + N_2 + H_2O + OH^- \qquad ..(48)$$

$$3\,NH_2OH \longrightarrow NH_3 + N_2 + 2H_2O \qquad ..(49)$$
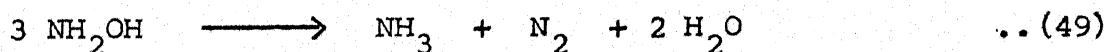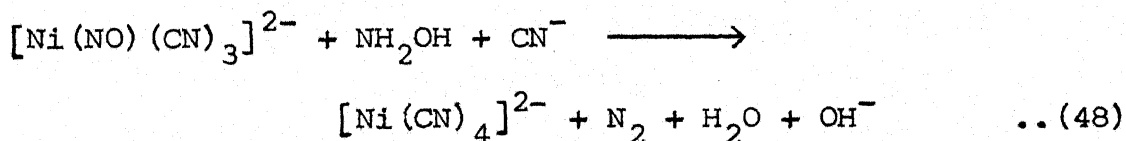
Thus this work contradicts the suggestion made earlier for the involvement of NO^- in these reactions. If NO^- is not the species formed by the reaction of hydroxylamine with strong alkali for the reductive nitrosylation, then hydroxylamine can nitrosylate in neutral or even in acidic medium. To put it to test, Sarkar and Mueller [47] recently attempted the reductive nitrosylation of several oxometallate anions using hydroxylamine. Taking thiocyanate as a coligand they were able to isolate species like $[Cr(NO)(NCS)_5]^{3-}$, $[Mo(NO)(CNS)_4(CH_3)_2NCO)]^{2-}$ and $[Os(NO)(NCS)_5]^{2-}$. It is interesting to note that hydroxylamine hydrochloride is used as such in these cases, which is suggestive enough to say that the reaction medium is slightly acidic in nature.

Wieghardt and coworkers reacted pentavalent and trivalent vanadium compounds with hydroxylamine in alkaline medium to get $[(dipic)V(NO)(NH_2O).H_2O][102]$. Contrary to these they observed that MoO_4^{2-} in the presence of terpyridine, reacts with hydroxylamine in acidic medium to form $[(terpy)Mo(NO)(NH_2O).H_2O]^{2+}$ [103]. Both the above reactions suggest that hydroxylamine functions as a nitrosylating reagent in alkaline as well as in acidic medium. The interesting part of this work lies in the fact that hydroxylamine can deprotonate to give a bidentate hydroxylamido(-1) ligand. The same authors have shown [103] that this hydroxylamido group can be further deprotonated to function as bidentate hydroxylamido(-2) group. It is interesting to

correlate the suggestion made by kinetic studies on the formation of $[Ni(NO)(CN)_3]^{2-}$ that hydroxylamine first gets coordinated and then deprotonated to generate the nitrosyl group [101]. However, from the synthetic point of view it has been shown recently that in the presence of good bidentate ligands only $\{Mo(NO)\}^4$ moiety can be trapped to give $K_3[Mo(NO)C_2O_4)_3]$ [104]. This is important in the sense that the bidentate hydroxylamido group can be treated as a 3 electron donor [105].

The complexes synthesized by the hydroxylamine method in any pH condition invariably contains a linear M-N-O group, whenever structural data were obtained. Thus the nitrosyl group can be regarded here as a three-electron donor or NO^+ which should be unstable in alkaline medium due to nucleophilic attack, and would be stable in acidic medium. The $\{Mo(NO)\}^6$ moiety in $K_4[Mo(NO)(CN)_5]$ is stable in strong alkaline medium. In neutral medium aerial oxidation of this leads to $(Ph_4P)_3[Mo(NO)(CN)_5].2H_2O$ [47] whereas in strong hydrochloric acid, this gives $Cs_2[Mo(NO)Cl_4.H_2O]$ [48] and $Cs_2[Mo(NO)Cl_5]$ [107]. In metal nitrosyl compounds, Hofmann and coworkers [64] have shown that the π-orbitals on the NO ligand are polarised such that there is an increase in electron density at the O-atom rather than the N-atom. Thus, in M-N-O moiety, potential electrophilic behaviour at N and nucleophilic at O is anticipated. However, the insensitivity of the Mo-N-O group to H^+ and OH^- shows the apparent incompleteness to understand the variation of electron density on the linear M-N-O group.

Scope of the Work

The activity of molybdenum in the natural systems is comprised of different oxidation states. The origin of the molybdenum activity involved in such reactions, essentially rests on the key role of MoO_4^{2-} (VI). Probably, the stability of this anion in a wider pH range (suitable for biological activities of molybdenum in metalloproteins) along with its readiness to enhance the coordination number and its ready reducibility accounts for its biological role as a sole representative of heavier transition metals. Amongst all the molybdoproteins known till date, the nitrogenase is the most difficult one to prepare. It is because if one believes that molecular nitrogen is going to attach with the molybdenum centres in nitrogenase using back-bonding scheme, molybdenum should be in lower oxidation states. Unfortunately our present chemical knowledge about the aqueous chemistry of the lower oxidation states of molybdenum is very meagre (vide supra). In view of this it would be highly interesting to explore the possibilities of reducing hexavalent-molybdenum to the lower ones (O, I, II) in aqueous media. Furthermore the possibility of using a suitable reducing reagent can be explored in such a way as to give a hint for the reduction of the hexavalent molybdate in natural systems.

Recently, it has been shown by Egami and coworkers [109] that molybdate(VI) catalyses the reaction between hydroxylamine and formaldehyde (Oro's synthesis) to generate aminoacids in

modified sea medium. They tried to mimic the prebiotic chemistry regarding the possible roles of simple compounds (HCHO and NH_2OH) in the synthesis of essential aminoacids using HCN as the precursor intermediate (Strecker's synthesis). It is very unlikely that the hexavalent molybdenum can be a stable species in the reducing prebiotic atmosphere. Furthermore, to get the final products they suggested some successive dehydration steps which are carried out in aqueous medium (modified sea medium):

$$HCHO + NH_2OH \longrightarrow CH_2NOH + H_2O \qquad ..(50)$$

$$CH_2-NOH \longrightarrow HCN + H_2O \qquad ..(51)$$
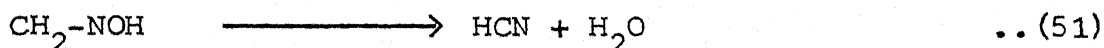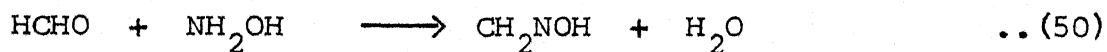
It is well known that many oxometallate anion can be reductively nitrosylated using alkaline hydroxylamine/KCN. Recently, it has been shown that hydroxylamine alone is capable of reductive nitrosylation without cyanide and even in neutral or acidic medium (vide supra). Interestingly when molybdate is taken as the oxometallate anion the "alkaline-hydroxylamine method" yields $K_4[Mo(NO)(CN)_5]$ which can be regarded as a zero-valent molybdenum compound (vide supra). On the other hand, using nearly neutral or slightly acidic conditions, nitrosyl-molybdenum(III) moiety would be formed. Hence it would be highly interesting to explore in detail the specificity of hydroxylamine to generate nitrosylmolybdenum moieties in varied pH range. These reactions would also help to understand the

exact species responsible for the catalytic activity of Egami's work.

Besides, dinitrosylmolybdenum species ${Mo(NO)_2}^6$ are also synthesized using nonaqueous chemistry under inert atmosphere [66,67a,67b]. Essentially in all the reactions, $Mo(CO)_6$ has been used as the source of molybdenum. These dinitrosylmolybdenum species can be regarded as containing formal zerovalent molybdenum. Contrary to these, alkaline hydroxylamine gives mononitrosylmolybdenum moiety in the same oxidation state. It has been observed that $MoCl_5$ can be nitrosylated stepwisely to give ${Mo(NO)}^4$ and ${Mo(NO)_2}^6$ using nitric monoxide [67]. Hence the possibility of dinitrosylation of molybdenum using hydroxylamine can be explored which should have some bearing with the pH of the medium and with the presence of coligand. It would also be interesting to explore any interconversion of the two species. The ${Mo(NO)}^4$ moiety should behave like ${V(NO)}^4$ (as in $K_3[V(NO)(CN)_5]$) and it has already been shown that ${V(NO)}^4$ group can disproportionate to give ${V(NO)_2}^6$ and some denitrosylated V(II) and V(III) species [110].

Another important aspect of the nitrosyl chemistry of molybdenum stems from a series of interesting reactions whereby cluster compounds, especially compounds containing Mo-Mo multiple bonds, where these metal-metal bonds can be completely broken by inserting nitrosyl groups [70,71]. As such these reactions are irreversible. At this point it would

be of great interest to see that by some experimental skill the
nitrosylmolybdenum moieties can be denitrosylated to give simple
monomeric compounds or dimeric or higher aggregation with the
involvement of metal-metal bond.

On the whole, synthetic manipulation or the studies of the
reactions involved herein is straight forward. The recent
finding of catalytic activity for these nitrosyl derivatives
in homogenous systems is exciting [112]. Some unusual reactions
such as that of alkyl substituent on the double bond appears to
migrate to form all possible combinations in alkene [112]. The
actual mechanism of such reactions is problematic to elucidate.
However, newer unusual reactivity of these nitrosyl species may
exist. And exploration of some reactions along these lines may
be difficult, but exciting.

In the view of our relatively poor knowledge and under-
standing about the chemistry of molybdenum in its lower oxida-
tion states it is of extreme interest to explore the possibility
of formation of such compounds especially in aqueous and aerobic
media and interpretation of their properties which may lead to
some understanding with relevance to the nitrogenase enzyme.
The interaction of the molybdate and hydroxylamine invariably
generates nitrosylmolybdenum species and as recent   structural
investigation of some of these compounds has shown the linearity
of Mo-N-O attachment, one can presume these nitrosyl complexes
containing nitric monoxide as NO^+. NO^+ is isoelectronic to N_2

and in such a way that the chemistry of these nitrosyl deriva-
tives of molybdenum especially in aqueous medium would help to
understand the role of molybdenum in nitrogen fixation.
A representative example of the nitrosylmolybdenum compounds
have been presented in Table I.

From Table I, it is apparent that the compound containing
$\{Mo(NO)\}^4$ moiety have some special feature which is uncommon to
any other configuration. Contrary to the suggestions made by
Stiefel [112] the complexes containing the $\{Mo(NO)\}^4$ moiety
do not rigorously obey the 18 electron rule. This apparent
anomaly can be easily explained by following an energy level
diagram of all the possible stereochemistries containing this
electronic configuration (vide infra). However, this change
over in coordination number is strongly suggestive of this
configuration to act as a potential catalytic moiety.

TABLE I

'd' Electron configuration	Coordination number	Example	Ref.
d^6	6	$K_4[Mo(NO)(CN)_5]$	[64]
d^5	6	$(Ph_4P)_3[Mo(NO)(CN)_5]$	[47]
		$Cs_2[Mo(NO)Cl_4 \cdot H_2O]$	[48]
d^4	5	$(PPh_4)[Mo(NO)Cl_4]$	[107]
	6	$Cs_2[Mo(NO)Cl_5]$	[107]
	7	$[Mo(NO)(DTC)_3]$	[114]

Thus the studies on these complexes of molybdenum whereby the oxidation state varies from II to I to O would be an interesting aspect even from the bioinorganic point of view as it can be traced that enzymatic molybdenum can change at the most three oxidation states during its catalytic behaviour [115].

Keeping these views in mind, some ligands having good complexing abilities with the change in donor site to nitrogen, oxygen, and sulphur were tried as coligands. Depending on the nature of neutral or negative ligands with the varying charges on the nitrosylmolybdenum moieties, complexes consisting of cationic, nonelectrolytic and anionic type as well can be synthesized. In this series the variation of the chemical properties can be enlightened using the interpretative nature of the existing physicochemical studies.

2.1A Elemental Analysis

The elements carbon, hydrogen and nitrogen were estimated by standard microanalytical methods. The procedure for estimation of chlorine, and sulphur follows:

Chlorine:

The amount of chlorine present in any complex was determined by fusing a known weight of the sample in a nickel crucible with about 20 times of a mixture of Na_2CO_3 and $NaNO_3$. Heating was continued till a clear melt was produced. It was kept for five minutes in molten condition, cooled and then taken up with water and filtered. The filtrate was made acidic with 1% nitric acid and boiled for 10 minutes. How Any precipitate appeared at this stage was filtered in a previously weighed sintered crucible, washed with very dilute nitric acid till free from excess silver ions, dissolved in ammonium hydroxide, reprecipitated with nitric acid and finally weighed as silver chloride by drying at 110°C.

Sulphur:

The complex containing sulphur was decomposed by using
sodium carbonate, sodium nitrate mixture as described above in
the estimation of chlorine. The resulting mass was extracted
with water and bromine water was added and the solution was
heated on a water-bath for 1 hour. The solution was then
treated with dilute hydrochloric acid. Any precipitate that
appeared at this stage was filtered off and the sulphate in the
filtrate was estimated as barium sulphate in the usual manner.

2.1B Identification of Coordinated Nitrosyl Group in Complexes by Chemical Method

Amongst the methods normally applied to characterize
coordinated nitric oxide, IR technique is the most widely used.
However, nitric oxide coordinated complexes having very low
ν_{NO} sometimes pose problems in diagnosing the IR stretching
frequency ν_{NO}. The situation may become worse when the
complexes are isolated in certain media, like ketones which
have a functional group absorbing strongly in the same region
as NO in the infrared. Hence a chemical test was developed to
identify the coordinated nitric oxide quickly. The principle
involved in this method is the exploitation of the electrophilic
behaviour of coordinated nitric oxide group. The linearly bound
M-N-O group may be assumed to contain 'NO$^+$', which can react
with strong alkali to produce NO_2^-. The formation of NO_2^- can

be effectively tested by using Greiss's reagent[111] provided complexes under study do not contain any NH_2OH, NO_2^- or NO_3^- ligands. Added difficulty is encountered when coordinated nitric monoxide is attached to a metal ion in very low formal oxidation states, for example, in complexes containing $\{Mo(NO)_2\}^6$ moiety. Once coordinated NO^+ has been converted into NO_2^-, the molybdenum is now in very low oxidation state which is sufficiently powerful to reduce NO_2^- to NH_3. Due to this reason the decomposition of compounds using alkali were done in boiling water-bath conditions. The reduction of generated NO_2^- to ammonia by naked metal ion was avoided by reducing the digestion time and monitoring the reduction stage using Nessler's reagent. The reaction mixture was then cooled and centrifuged and the centrifugate was cooled in ice-water, cautiously acidified with acetic acid and Greiss's reagent was added into it to get a deep reddish-violet colour immediately (some times precipitation appeared on acidification which did not affect the test). In order to standardise the method several nitric oxide coordinated compounds were employed. Some examples are given in Table 2.1.

All the mononitrosyl derivatives of molybdenum described in the thesis can be converted into red orange $Cs_2[Mo(NO)Cl_5]$ in concentrated hydrochloric acid, where the compound is insoluble in aqueous medium, it can be dissolved in acetone and the test can be performed. As an example, the dtc derivative of

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TABLE 2.1

Sl.No.	Compound	Colour in Alkaline medium	Colour on acidi-fication with dil. acetic acid	Colour on addition of Greiss's reagent
1.	$Na_2[Fe(NO)(CN)_5]$	Pale yellow	Green	Deep reddish violet
2.	$K_3[Cr(NO)(CN)_5]$	"	Yellow	"
3.	$K_3[Mn(NO)(CN)_5]$	Colourless	Colourless	"
4.	$[Re(NO)(bipy)Cl_3]$	"	"	"
5.	$[Mo(NO)_2Cl_2(Py)_2]$	"	"	"
6.	$Cs_2[Mo(NO)_2Cl_4]$	"	"	"
7.	$Cs_2[Mo(NO)Cl_5]$	"	"	"
8.	$[Mo(NO)Cl(o\text{-}phen)_2]Cl$	"	"	"
9.	$[W(NO)_2Cl_2(Py)_2]$	"	"	"

$\{Mo(NO)\}^4$ moiety can be dissolved in acetone and the resulting solution on mixing with concentrated hydrochloric acid containing CsCl and on prolonged warming gave the precipitate of $Cs_2[Mo(NO)Cl_5]$. The method is very rapid when compounds soluble in concentrated hydrochloric acid are taken.

In the case of dinitrosyl derivatives of molybdenum, the corresponding cesium salt of $[Mo(NO)_2Cl_4]^{2-}$ is fairly stable in hydrochloric acid and can be extracted with acetone containing hydrochloric acid. The cesium salts of other anionic molybdenum complexes for example $[Mo(NO)Cl_5]^{2-}$ or $[MoOCl_5]^{2-}$ are not soluble in the same medium. Thus any dinitrosyl molybdenum derivative can be treated with concentrated hydrochloric acid containing CsCl and on evaporation followed by extracting the mass using acetone-hydrochloric acid mixture (20:1 ml), $Cs_2[Mo(NO)_2Cl_4]$ can be separated. The only exception for these two tests is the tetraphenylphosphonium salt containing thiocyanato complexes of the respective moiety.

2.2 Complexes with $\{Mo(NO)_2\}^6$ Moiety

Dichlorodinitrosyl bis(pyridine)molybdenum(0), $[Mo(NO)_2Cl_2(Py)_2]$ (1)

Ammonium heptamolybdate (1.0 g) and hydroxylamine hydrochloride (1.7 g) were taken in pyridine glacial-acetic acid mixture (7 ml; 10 ml) and slowly digested at 105°C for an hour to get a greenish brown solution. Twenty ml of concentrated

hydrochloric acid was added to it to get a clear green solution which was poured into 250 ml of boiling water. The resulting solution was kept below the boiling point for an hour and a lemon green product thus formed was allowed to settle overnight. It was filtered, washed with dilute hydrochloric acid and finally with water and air-dried and analysed. Yield, 440 mg; decomposes above 180°C.

Anal. Calcd for $MoC_{10}H_{10}N_4O_2Cl_2$: C, 31.16; H, 2.59; N, 21.80; Cl, 18.44%. Found: C, 31.27; H, 2.85; N, 21.88; Cl, 18.24%.

Dichlorodinitrosyl bis(γ-picoline)molybdenum(0), $[Mo(NO)_2Cl_2(γ-pic)_2]$ (2)

This complex was synthesized as described above using γ-picoline instead of pyridine. Yield, 525 mg, decomposes above 150°C.

Anal. Calcd for $MoC_{12}H_{14}N_4O_2Cl_2$: C, 34.85; H, 3.4; N, 13.56; Cl, 17.17%. Found: C, 34.14; H, 3.69; N, 13.1; Cl, 16.90%.

Dichloro bis(β-picoline)dinitrosylmolybdenum (0) $[Mo(NO)_2Cl_2(β-pic)_2]$ (3)

The β-picoline derivative was also prepared in an analogous manner by replacing γ-picoline by β-picoline; yield, 575 mg; decomposes above 150°C.

Anal. Calcd for $MoC_{12}H_{14}N_4O_2Cl_2$: C, 34.85; H, 3.4; N, 13.56; Cl, 17.17%. Found: C, 35.06; H, 2.81; N, 13.3; Cl, 16.85%.

Attempted Preparation of $[Mo(NO)_2Cl_2(\alpha-pic)_2]$ and $[Mo(NO)_2Cl_2(quinoline)_2]$

When α-picoline or quinoline was used to synthesize the corresponding dinitrosylmolybdenum(0) compounds using the method described earlier, no analogous complex were formed.

Bis(dimethyldithiocarbamato)dinitrosylmolybdenum(0), $[Mo(NO)_2(Me_2dtc)_2]$ (4)

Ammonium heptamolybdate (1.0 g) and hydroxylamine hydrochloride (1.7 g) were heated in 10 ml dimethylformamide slowly and with shaking at 90°C. The solution slowly changed from colourless to yellow, brown and finally to green colour (care was taken to avoid vigorous heating and exothermic reaction while the solution changes from brown to green colour). The solution was cooled to room temperature and a solution of sodium dimethyldithiocarbamate dihydrate (2.1 g) in ice-cold water (200 ml) was added while stirring. A brown precipitate thus formed was allowed to settle for an hour. The solid was separated and extracted with diethyl ether (200 ml). On evaporation the crude product was obtained. This was recrystallized from methanol. The recrystallized product was further purified by column chromatograph (silica gel, 60-120 mesh) using $CHCl_3$ as

the eluent. Yield, 1.0 g; decomposes above 275°C.

Anal. Calcd for $MoC_6H_{12}N_4S_4O_2$: C, 18.35; H, 3.75; N, 13.85; S, 32.85%. Found: C, 18.16; H, 3.03; N, 14.14; S, 32.32%.

Bis(diethyldithiocarbamato)dinitrosylmolybdenum(0), $[Mo(NO)_2(Et_2dtc)_2]$ (5)

The title compound was prepared as described above, using diethyldithiocarbamate dihydrate (2.6 g) instead of dimethyl-dithiocarbamate. Yield, 850 mg; m.p. 127°C (lit.[114] 127-28°C).

Anal. Calcd for $MoC_{10}H_{20}N_4S_4O_2$: C, 26.56; H, 4.43; N, 12.38; S, 28.32%. Found: C, 26.23; H, 5.20; N, 12.05; S, 28.45%.

Bis(cysteine)dinitrosylmolybdenum(0), $[Mo(NO)_2(cysteine)_2]$ (6)

Ammonium heptamolybdate (1.0 g) and hydroxylamine hydro-chloride (1.7 g) were heated in 10 ml dimethylformamide at 90°C, slowly with constant stirring to get a green solution which was kept at 60°C for about 15 minutes. Cysteine (1.5 g) dissolved in hot water (250 ml) was added into the green solution and the resultant mixture was kept at its boiling point temperature for about 90 minutes. The solution was kept for 48 hours at room temperature whereby a dark green compound separated. This was filtered, washed with water, followed by methanol and air dried. Yield, 375 mg; decomposes above 150°C.

Anal. Calcd for $MoC_6H_{12}N_4O_6S_2$: C, 18.18; H, 3.0; N, 15.16; S, 16.17%. Found: C, 18.02; H, 2.67; N, 14.75; S, 15.85%.

Bis(acetylacetonato)dinitrosylmolybdenum(0), [Mo(NO)$_2$(acac)$_2$] (7)

Ammonium heptamolybdate (1.0 g) and hydroxylamine hydro-chloride (1.7 g) were heated in 10 ml dimethylformamide at 90°C, slowly with constant stirring to get a green solution which was kept at 60°C for about 15 minutes. A solution of acetylacetone (2 ml) in 15 ml of methanolic-KOH (1.3 g) was added and the resulting mixture was refluxed for an hour and poured into 250 ml of boiling water. On keeping at ca. 90°C for 30 minutes, the desired product started separating as a green solid. The mixture was allowed to cool and the precipi-tate was filtered, washed with water and dried. The crude product was purified by column chromatograph (silica gel, 60-120 mesh), using benzene as eluent. Yield, 600 mg; m.p., 156° (lit.[141], 146-147°C).

Anal. Calcd for $MoC_{10}H_{14}N_2O_6$: C, 33.89; H, 3.95; N, 7.90%. Found: C, 34.75; H, 3.87; N, 8.00%.

Dichloro(o-phenanthroline)dinitrosylmolybdenum(0), [Mo(NO)$_2$Cl$_2$(o-phen)] (8)

Ammonium heptamolybdate (1.0 g) and hydroxylamine hydro-chloride (1.7 g) were heated in 10 ml dimethylformamide slowly with constant stirring to obtain green solution which was kept at 60°C for about 15 minutes. This was cooled to room temperature

and 20 ml of acetonitrile was added to it. The mixture was
filtered under suction. To the filtrate, 2.0 g of o-phenan-
throline was added and the mixture was stirred for 2 hours in
a closed vessel. Twenty ml of concentrated hydrochloric acid
was added, any residue appeared at this stage was filtered off.
The filtrate was evaporated to 10 ml under reduced pressure
whereby a bright green compound separated. This was recrysta-
llized in chloroform. Yield, 925 mg; decomposes above 180°C.

Anal. Calcd for $MoC_{12}H_8N_4O_2Cl_2$: C, 35.4; H, 1.96;
N, 13.76; Cl, 17.43%. Found: C, 36.02; H, 2.3; N, 13.5;
Cl, 16.8%.

(2,2'-Bipyridyl)dichlorodinitrosylmolybdenum(0), $[Mo(NO)_2(bipy)Cl_2]$ (9)

This was synthesized as described above using 2,2'-bipyri-
dyl (1.7 g) instead of o-phenanthroline, yield: 800 mg;
decomposes above 180°C.

Anal. Calcd for $MoC_{10}H_8N_4O_2Cl_2$: C, 31.34; H, 2.09;
N, 14.64; Cl, 18.51%. Found: C, 30.85; H, 2.65; N, 14.68;
Cl, 17.90%.

Cesium tetrachlorodinitrosylmolybdenum(0), $Cs_2[Mo(NO)_2Cl_4]$ (10)

Powdered ammonium heptamolybdate (1.0 g) and hydroxyl-
amine hydrochloride (1.7 g) were taken in 25 ml water and the
reaction mixture was heated at 60°C till the red orange preci-
pitate separated out. The mixture was kept for 30 minutes at

room temperature with stirring. The reaction mixture was finally warmed to dissolve the precipitate resulting in a red brown solution. Few drops of concentrated hydrochloric acid was added to it and the colour was changed to green and then 25 ml of concentrated hydrochloric acid was added. The solution was boiled for an hour and CsCl (2.0 g) was added to it. The resultant solution was evaporated to 10 ml and cooled. The green crystalline compound separated out was extracted in concentrated hydrochloric acid-acetone mixture (2:20 ml) and kept over solid KOH in a vacuum desiccator for crystallization. The crystals were filtered, washed with ether and dried. Yield, 650 mg; decomposes above 200°C.

Anal. Calcd for $Cs_2MoN_2O_2Cl_4$: N, 5.0; Cl, 25.15%. Found: N, 5.2; Cl, 25.36%.

Tetraethylammonium tetracyanodinitrosylmolybdenum(0), $[(C_2H_5)_4N]_2[Mo(NO)_2(CN)_4]$ (11)

Ammonium heptamolybdate (1.0 g) and hydroxylamine hydrochloride (1.7 g) were heated together in 10 ml dimethyl formamide slowly with constant stirring to obtain green solution which was kept at 60°C for about 15 minutes. This was cooled to room temperature and 30 ml of acetonitrile was added to it. The mixture was filtered under suction. To the filtrate, an excess of sodium cyanide (4.0 g) was added and stirred at room temperature for about 4 hours. The unreacted NaCN was filtered off and to the filtrate tetraethylammonium chloride (1.5 g) was added.

The mixture was stirred for an hour and filtered to remove any residue at this stage. The filtrate was allowed to evaporate at room temperature whereby bright green compound separated which was filtered, washed with methanol and finally with ether and dried. Yield, 850 mg; decomposes above 150°C.

Anal. Calcd for $MoC_{20}H_{40}N_8O_2$: C, 46.17; H, 7.6; N, 21.05%. Found: C, 46.48; H, 6.42; N, 20.4%.

Tetraphenylphosphonium tetrathiocyanatodinitrosylmolybdenum $[PPh_4]_2[Mo(NO)_2(NCS)_4]$ (12)

To the green acetonitrile solution which was obtained as described above, KNCS (5 g) was added and the mixture was stirred for about 3 hours. The unreacted KNCS was filtered off and to the filtrate, tetraphenylphosphonium chloride (4.0 g) was added. The clear brown red solution was allowed to evaporate at room temperature. The brown-black precipitate was filtered, washed with water and finally with methanol and dried. The dry solid was dissolved in 4-5 ml dimethylformamide and filtered to free it from any traces of residue and into the filtrate, 20 ml methanol was added for crystallization. After a week, green octahedrally shaped single crystals were separated which were filtered, washed with methanol and dried. Yield, 2.150 g; decomposes above 180°C.

Anal. Calcd for $MoC_{52}H_{40}N_6O_2S_4P_2$: C, 58.4; H, 3.74; N, 7.86; S, 11.98%. Found: C, 58.65; H, 3.65; N, 7.63; S, 12.35%.

Tetraethylammonium bis(oxalato)dinitrosylmolybdenum(0), $[(C_2H_5)_4N]_2[Mo(NO)_2(C_2O_4)_2]$ (13)

Into the green acetonitrile solution obtained as described above, oxalic acid (3.5 g) was added and stirred for ca. 3 hours. The unreacted oxalic acid was removed by filtration and to the filtrate, tetraethylammonium chloride (4.0 g) was added. The clear solution was allowed to concentrate over P_2O_5 desiccator under vacuum to 10 ml whereby bright green compound separated out. This was filtered, washed with water several times and finally with methanol and dried over P_2O_5; yield, 750 mg; decomposes above 200°C.

Anal. Calcd for $MoC_{20}H_{40}N_4O_{10}$: C, 40.54; H, 3.38; N, 9.45%. Found: C, 40.42; H, 4.50; N, 10.25%.

Properties of the Complexes Containing $\{Mo(NO)_2\}^6$ Moiety

All the prepared complexes containing $\{Mo(NO)_2\}^6$ moiety are green excepting dialkyldithiocarbamato derivatives which are golden brown in colour. Most of the derivatives are insoluble in water and amongst the ionic compounds, $[(Et)_4N]_2[Mo(NO)_2(CN)_4]$ and $Cs_2[Mo(NO)_2Cl_4]$ are soluble in water. In conformity to previously reported studies [114], $[Mo(NO)_2(R_2dtc)_2]$ are highly soluble in most of the organic solvents. In solution they are appreciably stable but in presence of light decomposition occurs. Except $[Mo(NO)_2Cl_2(Py)_2]$, complexes with picolines and aromatic diimines are sparingly soluble in CH_2Cl_2 and $CHCl_3$.

[Mo(NO)$_2$(cysteine)$_2$] is insoluble in most of the organic solvents in contrast to [Mo(NO)$_2$(acac)$_2$] which is soluble even in petroleum ether (60-80°C). All the compounds are fairly stable in solid state. They undergo decomposition in alkaline solution. The derivatives of the aromatic heterocyclic bases are most stable, and they remain unaffected in warm concentrated nitric acid. For the picoline derivatives the methyl group also remains unaffected under this conditions.

2.3   Complexes with {Mo(NO)}^{5} Moiety

Cesium aquatetrachloronitrosylmolybdenum(I), Cs$_2$[Mo(NO)Cl$_4$].H$_2$O (14)

Freshly prepared K$_4$[Mo(NO)(CN)$_5$].2H$_2$O [64] (2.0 g) was added to concentrated hydrochloric acid (50 ml) and refluxed at its boiling point for about 20 minutes in oxygen-free atmosphere to get a clear wine red to green colour. Cesium chloride (1.8 g) was added to it and the mixture was refluxed for another ca. 20 minutes and filtered quickly. To the green filtrate, methanol (25 ml) and diethyl ether (25 ml) were added and kept in a desiccator containing methanol-diethyl ether (50:50). After a week, dark bluish green crystals separated which were filtered, washed with methanol and finally with ether and dried over KOH; Yield, 450 mg; decomposes above 150°C.

Anal. Calcd for Cs$_2$MoCl$_4$NO$_2$H$_2$: H, 0.31; N, 2.18; Cl, 22.09%. Found: H, 1.20; N, 2.35; Cl, 23.50%.

Anal. Calcd for $MoC_{20}H_{16}N_5Cl_2O$: C, 47.16; H, 3.14; N, 13.76; Cl, 13.93%. Found: C, 49.34; H, 2.85; N, 13.25; Cl, 13.68%.

Properties of the Complexes Containing $\{Mo(NO)\}^5$ Moiety

Complexes containing $\{Mo(NO)\}^5$ moiety are least stable among the molybdenum nitrosyl complexes described in this thesis. All these compounds are very much susceptible to air oxidation. In water they dissolve slowly to give pink colour which quickly changes to green. In concentrated hydrochloric acid the cationic complexes are fairly soluble. The colour change from pink to green is faster in presence of oxygen. In deoxygenated water or dilute hydrochloric acid the pink colour persists for a longer time. The pink solution under oxygen changes to green which on slow evaporation gives a deep green compound. In concentrated hydrochloric acid this compound changes to the well known orange red $Cs_2[Mo(NO)Cl_5]$ suggesting strongly a different composition for the green compound. This is highly paramagnetic in nature and has not given any ESR signal at room temperature contrary to the starting compound. This implies that molybdenum present in this compound may be in +3 oxidation state. However, it is difficult to get the compound in a pure form and hence other studies have not been attempted.

2.4 Complexes with {Mo(NO)}^{4} Moiety

Cesium pentachloronitrosylmolybdenum(II), $Cs_2[Mo(NO)Cl_5]$ (17)

Ammonium heptamolybdate (1.0 g) was dissolved in 20 ml water and 1.3 g of hydroxylamine hydrochloride was added to it and heated at 60-65°C. The red orange precipitate initially formed slowly disappeared and the solution turned brown. Cesium chloride dissolved in concentrated hydrochloric acid (40 ml) was added to it and the mixture was heated at boiling temperature and within 5 minutes, a bright, shining red brown crystals of $Cs_2[Mo(NO)Cl_5]$ started separating. After another 5 minutes of heating, the reaction mixture was allowed to cool to room temperature. The crystals thus formed were filtered, washed with methanol and ether and dried over KOH desiccator. Yield, 1.45 g.

Anal. Calcd for $Cs_2MoNOCl_5$: N, 2.46; Cl, 31.13%. Found: N, 2.52; Cl, 31.80%.

Potassium hydroxylamido(-1)tetrathiocyanatonitrosylmolybdenum(II), $K_2[Mo(NO)(NH_2O)(NCS)_4]$ (18)

Ammonium heptamolybdate (1.0 g) with hydroxylamine hydrochloride (1.7 g) in 7 ml dimethylformamide was heated with constant shaking. The colourless solution slowly changes to yellow which was filtered. To the filtrate KNCS (2 g) was added and the mixture was stirred for 30 minutes and then filtered. To the filtrate, methanol (15 ml) was added and the mixture was kept in a closed container. After a week, a bright yellow solid

separated which was filtered and washed with methanol and dried in air. Yield, 400 mg.

Anal. Calcd for $K_2MoC_4H_2N_6O_2S_4$: C, 10.25; H, 0.2; N, 17.94; S, 27.34%. Found: C, 10.40; H, 1.2; N, 17.48; S, 26.85%.

Tetraethylammonium hydroxylamido(-1)tetrathiocyanatonitrosylmolybdenum(II), $[(C_2H_5)_4N]_2[Mo(NO)(NH_2O)(NCS)_4]$ (19)

A mixture of ammonium heptamolybdate (4.0 g) and KNCS (20 g) was dissolved in water (250 ml) and heated at 80°C. Hydroxylamine hydrochloride (6.8 g) was added to the clear solution. An haziness in the mixture was removed by filtration and the clear filtrate was heated for about 90 minutes at 80°C. The solution was cooled to room temperature and into it, tetraethylammonium chloride (12 g) was added. A yellow, glassy semi-solid separated out and the same was washed several times with cold water whereby it solidified. The lump was taken with methanol (20 ml) and the solid was broken into a powder form which was filtered and dried. The solid was dissolved in acetonitrile (20 ml) and then precipitated by adding 40 ml methanol. The product was filtered, washed with water, methanol and finally with ether and dried. Yield, 9.6 g.

Anal. Calcd for $MoC_{20}H_{42}N_8O_2S_4$: C, 36.92; H, 6.46; N, 17.23; S, 19.69%. Found: C, 36.23; H, 5.84; N, 16.65; S, 18.85.

Tetraphenylphosphonium hydroxylamido(-1)tetrathiocyanatonitro-sylmolybdenum(II), [PPh_4]$_2$[Mo(NO)(NH$_2$O)(NCS)$_4$] (20)

A mixture of ammonium heptamolybdate (1.0 g) and KNCS (5.0 g) was taken in water (50 ml) and heated at 80°C. Hydro-xylamine hydrochloride (1.7 g) was added to the clear solution and the mixture was heated below its boiling point for 90 min. Tetraphenylphosphonium chloride (4.0 g) dissolved in methanol (20 ml) was added to the reaction mixture which was previously cooled to room temperature. The yellow glass like semi-solid formed was washed several times with cold water whereby it soli-dified. The lump was broken in methanol (20 ml) medium and the crude mass was filtered, washed with methanol and dried. The solid was dissolved in acetonitrile (20 ml) and precipitated by adding methanol (40 ml). The product was filtered, washed first with methanol, then with ether and finally dried. Yield, 4.9 g.

Anal. Calcd for MoC$_{52}$H$_{42}$N$_6$O$_2$P$_2$S$_4$: C, 58.43; H, 3.93; N, 7.87; S, 11.98%. Found: C, 60.20; H, 4.32; N, 7.53; S, 11.54%.

Hydroxylamido(-1)bis(o-phenanthroline)dithiocyanatonitrosyl-molybdenum, [Mo(NO)(NH$_2$O)(o-phen)$_2$(NCS)$_2$] (21)

[Et$_4$N]$_2$[Mo(NO)(NH$_2$O)(NCS)$_4$] (1.3 g) was dissolved in acetonitrile (10 ml) and heated at 60°C. o-Phenanthroline (800 mg) was added to it, the mixture was heated for about 15 minutes under reflux. The resultant solution was left over-night at room temperature whereby bright yellow crystals separa-ted out, which were filtered, washed with 20 ml acetonitrile and

finally with ether and dried. Yield 1.0 g.

Anal. Calcd for $MoC_{26}H_{18}O_2S_2$: C, 49.21; H, 2.84; N, 17.67; S, 10.09%. Found: C, 48.56; H, 3.67; N, 16.25; S, 9.80%.

Hydroxylamido(-1)bis(2,2'-bipyridyl)dithiocyanatonitrosyl-molybdenum(II), $[Mo(NO)(NH_2O)(bipy)_2(NCS)_2]$ (22)

The title compound was synthesized by above described method using 2,2'-bipyridyl (760 mg) instead of o-phenanthroline. Yield, 450 mg.

Anal. Calcd for $MoC_{22}H_{18}N_8O_2S_2$: C, 45.05; H, 3.07; N, 19.11; S, 10.92%. Found: C, 45.62; H, 3.65; N, 18.68; S, 10.38%.

Bis(N,N-dimethyldithiocarbamato)(N,N-dimethylmethyl(S)dithiocarba-mato)nitrosylmolybdenum(II), $[Mo(NO)(Me_2-dtc)_2(Me_2NCSSMe)]$ (23)

Ammonium heptamolybdate (1.0 g) was dissolved in 20 ml of warm water and to the clear solution, hydroxylamine hydrochloride (1.7 g) was added. The mixture was stirred for 30 minutes, whereby a red-orange precipitate separated. Acetone (120 ml) was added to the mixture and refluxed till the solid dissolved to give a clear solution. A saturated solution of sodium dimethyldithiocarbamate (3.6 g) in water-acetone (1:1) was added to it and the resultant mixture was refluxed till the red-brown solution changed to green in colour. It was cooled at room temperature and 250 ml of water was added to it. A bluish-green

compound precipitated which was filtered off, washed with water, finally with methanol and air dried. The compound was dissolved in chloroform (green colour) and was eluted through neutral or basic alumina (60-120 mesh) column. The eluted solution was bright yellow in colour, which on evaporation in air gave yellow crystals. These were collected and washed with petroleum ether (b.p. 60-80°C); yield, 850 mg.

Anal. Calcd for $MoC_{10}H_{21}N_4OS_6$: C, 23.95; H, 4.19; H, 4.19; N, 11.17; S, 38.32%. Found: C, 23.15; H, 3.69; N, 11.07; S, 38.62.

Bis(N,N --diethyldithiocarbamato)(N,N -diethylmethyl(S)dithiocarbamato)-nitrosylmolybdenum(II), [Mo(NO)(Et$_2$-dtc)$_2$(Et$_2$NCSSMe)] (24)

The title compound was synthesized by the above described method using N,N --diethyldithiocarbamate (4.0 g) instead of N,N -dimethyldithiocarbamate (m.p., 220°C); yield 1.2 g.

Anal. Calcd for $MoC_{16}H_{33}N_4OS_6$: C, 32.82; H, 5.54; N, 9.57; S, 32.82%. Found: C, 32.26; H, 4.20; N, 9.44; S, 31.60%.

Tris(N,N -di-n-propyldithiocarbamato)nitrosylmolybdenum(II), [Mo(NO)(n-Pr$_2$-dtc)$_3$] (25)

This compound was prepared by the method described above. N,N -di-n-propyldithiocarbamate (4.5 g) was used instead of N,N -dimethyldithiocarbamate; yield 1.5 g (m.p. 158°C)

Anal. Calcd for $MoC_{21}H_{42}N_4OS_6$: C, 38.53; H, 6.42; N, 8.56; S, 29.35%. Found: C, 38.62; H, 5.45; N, 8.23; S, 30.20%.

Tris(N,N -di-n-butyldithiocarbamato)nitrosylmolybdenum(II), [Mo(NO)(n-Bu$_2$-dtc)$_3$] (26)

Ammonium heptamolybdate (1.0 g) was dissolved in 20 ml of warm water and to the clear solution, hydroxylamine hydrochloride (1.7 g) was added. The mixture was stirred for 30 minutes, whereby a red orange substance separated. Acetone (120 ml) was added to the mixture and refluxed till the solid dissolved to give a clear solution. A saturated solution of sodium N,N -di-n-butyldithiocarbamate (5.0 g) in acetone-water (1:1) was added to the mixture and refluxed till the red brown solution changed to green in colour. It was cooled to room temperature and 250 ml of water was added to it. A bluish-green tarry-mass settled which was washed several times with water. The compound was dissolved in chloroform and was filtered through silica column (60-120 mesh). The bluish-green solution was then eluted through basic or neutral alumina (60-120 mesh) column. The eluted solution was yellow in colour which on evaporation in air yielded yellow crystalline compound; yield, 750 mg; m.p. 120°C.

Anal. Calcd for $MoC_{27}H_{54}N_4OS_6$: C, 43.9; H, 7.32; N, 7.59; S, 26.02%. Found: C, 44.2; H, 5.20; N, 6.92; S, 25.80%.

Properties of the Complexes Containing $\{Mo(NO)\}^4$ Moiety

All complexes of this moiety attached with hydroxylamido group $\{Mo(NO)(NH_2O)\}^{2+}$ are highly soluble in dimethylformamide and acetonitrile. They are insoluble in water, ethanol and diethyl ether. $[Ph_4P]_2[Mo(NO)(NH_2O)(NCS)_4]$ in dimethylformamide slowly changes colour from yellow to green from which $[Ph_4P]_2[Mo(NO)_2(NCS)_4]$ can be isolated. Amongst the dithio-carbamato complexes of this moiety the dimethylthiocarbamato complex is only sparingly soluble in chloroform whereas other derivatives are highly soluble. It is important to note that in the synthesis of these derivatives the use of acetone is essential. In the absence of acetone, depending on the reaction conditions a mixture of mono- and dinitrosyl-derivatives are formed. Acetone, not only prevents the formation of dinitrosyl moiety, but also presumably involves in the methylation of dimethyldithiocarbamate (vide infra). The octa-coordinated complexes $[Mo(NO)(NH_2O)(L-L)_2(NCS)_2]$ (L-L = O-phen, bipy) are soluble in dimethylformamide and only slightly in acetonitrile. The fact that the complex containing $\{Mo(NO)(NH_2O)\}^4$ moiety changes to $\{Mo(NO)_2\}^6$ moiety in dimethylformamide and the recent observation by Wieghardt and coworkers [103] that the facile deprotonation of coordinated hydroxylamido(-1) to hydroxylamino(-2) suggest that these octa-coordinated complexes might be formulated as hepta-coordinated (LLH)[Mo(NO)(NHO)(LL)(NCS)_2] Molar conductance of these compounds in acetonitrile ($\Lambda_M = 18$ mho.cm^2.mole^{-1} for bipy, $\Lambda_M = 16.3$ mho.cm^2.mole^{-1} o-phen

compound) suggest that they are non-ionic in nature. Thus the above anionic formulation or the cationic complex, $[Mo(NO)(NH_2O)(o-phen)_2(NCS)]^+$ are ruled out. This is supported further by their inactiveness in passing through ion exchangers. The interesting property of these octa-coordinated derivatives where the hydroxylamido group is only mono-dentate (vide infra) is that they do not give rise to any dinitrosyl derivatives as have been observed by starting from the hepta-coordinated complex, $[Ph_4P]_2[Mo(NO)(NH_2O)(NCS)_4]$, where the hydroxylamido group is chelated. This inertness to further deprotonation of monodentate hydroxylamido group is suggestive of preferential coordination through oxygen.

2.5A Electrophilic Character of Coordinated Nitrosyl in $[Mo(NO)_2(CN)_4]^{2-}$ *

$[Et_4N]_2[Mo(NO)_2(CN)_4]$ (1 g) was taken in a solution containing KOH (1.12 g) and KCN (1.3 g) and 50 ml of air-free aqueous methanol (10:40 ml) and refluxed under nitrogen atmosphere. The initial green colour of the solution changed to violet within an hour. 100 ml of air-free ethanol was added to it. On cooling, a violet compound separated out which was filtered under suction and washed with air-free methanol in portions, yield, 500 mg.

The compound was analysed and found to be $K_4[Mo(NO)(CN)_5]$. The infrared spectrum shows characteristic bands for ν_{NO},

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*S. Sarkar & P. Subramanian, J. Inorg. Nucl. Chem., 1981, 43, 202.

$1450 \ cm^{-1}$ (lit. [113], ν_{NO} . $1455 \ cm^{-1}$).

The same compound can be isolated in a two-step process starting from $[Mo(NO)_2Cl_2(Py)_2]$ as shown in the following Scheme:

$$[Mo(NO)_2Cl_2(py)_2] \xrightarrow[\text{MeOH}]{\text{KCN.}} [Mo(NO)_2(CN)_4]^{2-}$$

(A)   (B)

Aqueous KCN/KOH

$$[Mo(NO)(CN)_5]^{4-}$$

(C)
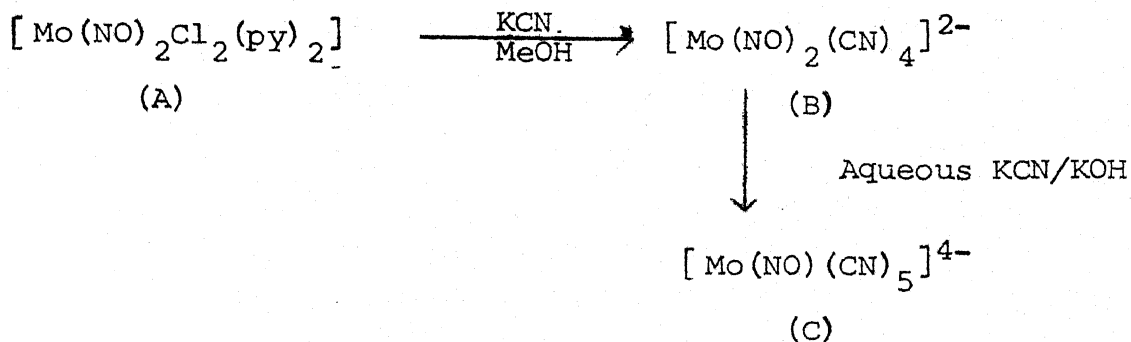
It is interesting to note that the conversion of (A) to (B) has been achieved only in the presence of cyanide and as long as there is no OH^- group, $[Mo(NO)_2(CN)_4]^{2-}$ species remains unchanged. The formation of this at this stage may be thought of as simple ligand displacement of Cl^- and pyridine by CN^-. However, the conversion of (B) to (C) requires the presence of KOH and water. A reasonable explanation for this step is that it is not a simple CN^- displacement reaction of 'NO^+', but responsible for the nucleophilic attack of OH^- at the coordinated nitrosyl in $[Mo(NO)_2(CN)_4]^{2-}$

An attempt has been made by Bottomley and coworkers [116-117] to correlate the ν_{NO} in metal nitrosyl complexes with the reactivity of coordinated nitrosyl groups by nucleophilic attack. They proposed that the metal nitrosyl compounds having

ν_{NO} < 1861 cm^{-1} will be susceptible to attack at the N-atom by nucleophiles. The compound under study is a dinitrosyl derivative and any correlation of this with a series of mononitrosyl complexes would not be useful. However, the conversion of $\{Mo(NO)_2\}^6$ moiety to $\{Mo(NO)\}^4$ has been studied by three different groups independently. Feltham and coworkers [118] first observed that cis-$[Mo(NO)_2(L-L)Cl_2]$ (L-L = diars or en) on keeping in methanol for several days changed to $[\{Mo(NO)(L-L)Cl_2\}_2N_2O_2]$. Coupling of two nitrosyl groups to form cis-hyponitrito complex, $[Pt(N_2O_2)(PPh_3)_2]$, has been structurally characterized [119]. The quantitative conversion of $[Mo(NO)_2(dtc)_2]$ into $[Mo(NO)(dtc)_3]$ by UV irradiation has been reported by Johnson and coworkers [120] with the assumption of the involvement of a dimeric hyponitrite intermediate. The conversion of $[Mo(NO)_2(dtc)_2]$ to $[MoL(dtc)_2(CH_3)_2SO(NO)]$ (L = N$_3^-$, NCO$^-$) in the presence of L in DMSO has been kinetically studied by Broomhead and coworkers [121] based on which the coupling of two molecules of reactive complex through a nitrosyl ligand on each complex to give a bridged hyponitrito species was suggested. Both groups of workers [120,121] have demonstrated that no liberation of any NO$^+$ took place during the course of reactions. Interestingly, Johnson and coworkers [120] have shown a dissociative pathway with the formation of a penta-coordinated intermediate species which has been deduced from the experimental observation. Contrary to this, an intermediate pentagonal bipyramidal complex with the association of the incoming ligand

L into the hexa-coordinated dinitrosyl species has been suggested by Broomhead and coworkers [121].

In the above mentioned reactions the formation of $\{Mo(NO)\}^4$ species resulted from the transfer of two electrons from each molybdenum towards one of the nitrosyl groups of the $\{Mo(NO)_2\}^6$ moiety which ultimately dimerizes with the formation of a bridged hyponitrite. In the present case, the conversion of $\{Mo(NO)_2\}^6$ to $\{Mo(NO)\}^6$ moiety is suggestive of no such electron transfer within Mo-N-O group. The yield of the product is above 60% with respect to the starting compound and no evolution of gas is noticed under the reaction conditions. The filtrate of the reaction product $K_4[Mo(NO)(CN)_5]$ gives a positive test for NO_2^- using Greiss's reagent. The test for nitrite is inconclusive in the sense that any nitrosyl compound having linear M-N-O attachment responds to the test and we are uncertain about the nature of the rest of the starting compound as that too responds to this test. However, if hyponitrite-bridged dinuclear complex is thought to be the intermediate compound with the ultimate formation of $K_4[Mo(NO)(CN)_5]$ for the present case, then the reaction should follow in the sequence:

$$\{Mo(NO)_2\}^6 \xrightarrow{-2\ e} \{Mo(NO)\}^4 \xrightarrow{+2\ e^-} \{Mo(NO)\}^6$$
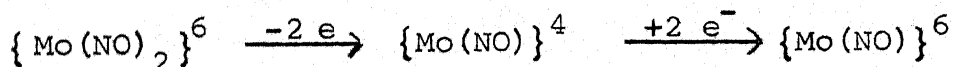
Thus, looking at the molybdenum, stepwise oxidation followed by reduction yields the ultimate product. As a check

for the second stage of the sequence, $\{Mo(NO)\}^4 \longrightarrow \{Mo(NO)\}^6$, a simple reaction like taking $[Mo(NO)Cl_5]^{2-}$ in aq. KCN/KOH was carried out. No nitrosyl derivative of molybdenum was obtained by this method and $\{Mo(NO)\}^4$ immediately decomposes in such an alkaline medium. The immediate decomposition of $\{Mo(NO)\}^4$ moiety in an alkaline medium suggests the instability of nitrosylmolybdenum group at this high pH. The air oxidation of $\{Mo(NO)\}^6$ to $\{Mo(NO)\}^5$ has been achieved only recently in aqueous (slightly basic) medium and though $\{Mo(NO)\}^5$ moiety can be stabilized in strong acid (vide supra), $\{Mo(NO)\}^4$ is not stable in alkaline media. The trends for the stability of $\{Mo(NO)\}^n$ (n = 6, 5, 4) is as follows:

stable in alkaline medium

$$\{Mo(NO)\}^4 \text{ —————— } \{Mo(NO)\}^5 \text{ —————— } \{Mo(NO)\}^6$$

stable in acidic medium
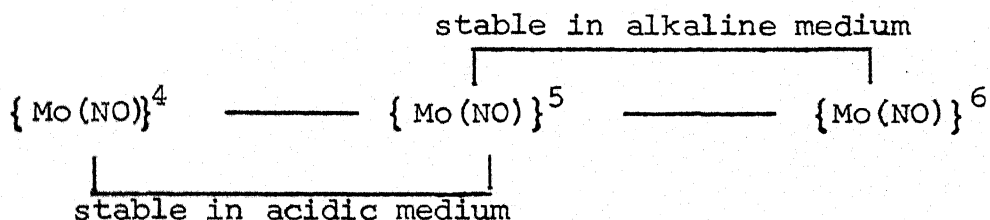
On the above grounds it may be inferred that the dinitrosylation reaction is not going analogously as have been observed earlier. The only alternative explanation for this reaction is the nucleophilic attack of OH$^-$ on the coordinated nitrosyl leading to the following reaction sequence:

$$[Mo(NO)_2(CN)_4]^{2-} \xrightarrow{\ 2\ OH^-\ } [Mo(NO)(CN)_4(NO_2)]^{4-} + H_2O$$

$$\downarrow CN^-$$
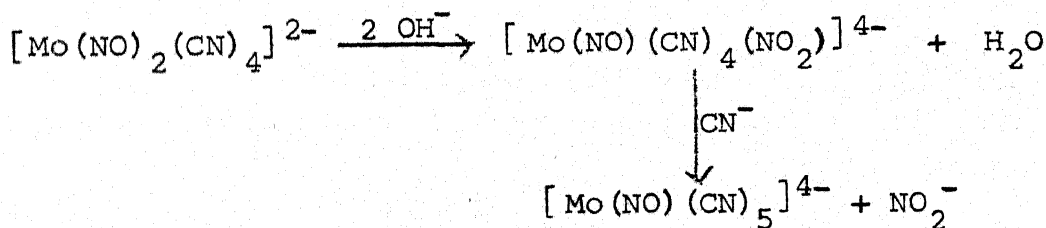
$$[Mo(NO)(CN)_5]^{4-} + NO_2^-$$

A kinetic study of this reaction would have given insight about the details of the mechanism. Unfortunately in solution $[Mo(NO)(CN)_5]^{4-}$ is susceptible to air oxidation in the presence of traces of oxygen and hence this study is awaited.

2.5B Denitrosylation of $\{MoNO\}^6$ Moiety

Ammonium hexachloromolybdenum(III), $[NH_4]_3[MoCl_6]$, (<u>27</u>)

$K_4[Mo(NO)(CN)_5] \cdot 2H_2O$ (2 g) was taken in an oxygen-free hydrochloric acid (100 ml) in which 2.5 g of tin was previously dissolved. The mixture was refluxed for about 45 minutes. Ammonium chloride (1.8 g) was added to it and heating was continued for another 15 minutes. A pale brown precipitate appeared at this stage and the contents were cooled to room temperature and suction-filtered. The filtrate was kept in a refrigerator for two days whereby a red-orange compound crystallized out. It was filtered, washed with methanol and ether, and dried. Yield, 800 mg.

Anal. Calcd for $MoN_3H_{12}Cl_6$: H, 3.20; N, 14.4; Cl, 56.77%. Found: H, 3.54; N, 14.8; Cl, 57.00%.

Denitrosylation of $\{Mo(NO)\}^4$ Moiety

Ammonium undecachlorodimolybdenum(IV), $[NH_4]_3[Mo_2Cl_{11}]$(<u>28</u>)

Ammonium heptamolybdate (1.0 g) and hydroxylamine hydrochloride (1.7 g) were taken in water (25 ml) and the mixture

was kept for 30 minutes with stirring. This mixture was then heated to get a clear solution and 2 drops of concentrated hydrochloric acid was added whereby it turned to a clear green colour. Concentrated hydrochloric acid (100 ml) was added to it and warmed for 20-30 minutes. Tin granules (2.0 g) were added to it and after complete dissolution, an excess of ammonium chloride (2.5 g) was added. After an hour (kept at room temperature), the precipitated material was filtered off, through a sintered glass funnel and the yellow-orange solution was kept in a closed container for overnight cooling. The separated yellow crystalline compound was filtered, washed with methanol and finally dried over P_2O_5; yield, 1.4 g.

Anal. Calcd for $Mo_2H_{12}N_3Cl_{11}$: H, 1.89; N, 6.60; Cl, 61.15%. Found: H, 2.60; N, 6.69; Cl, 61.05%.

Bis(o-phenanthroline)octachlorodimolybdenum(IV), $[Mo_2(o-phen)_2Cl_8]$ (29)

$[NH_4]_3[Mo_2Cl_{11}]$ (700 mg) was taken in a 20 ml conical flask containing 5 ml dimethylformamide. o-Phenanthroline (400 mg) was added and the reaction mixture was heated with stirring. The colour of the solution slowly changed to pink-violet and a white solid settled at the bottom. The solid was filtered and to the filtrate methanol (5 ml) was added and the mixture kept for overnight cooling. A pink-violet coloured crystalline compound separated out which was filtered, washed with water,

methanol and finally with ether and dried over P_2O_5 desiccator; yield, 860 mg.

Anal. Calcd for $MoC_{24}H_{16}N_4Cl_8$: C, 33.90; H, 1.87; N, 6.57; Cl, 33.3%. Found: C, 33.37; H, 1.76; N, 5.4; Cl, 32.8%.

Bis(2,2'-bipyridyl)octachlorodimolybdenum(IV), [$Mo_2(bipy)_2Cl_8$] (30)

$[NH_4]_3[Mo_2Cl_{11}]$ (700 mg) was taken in a 20 ml conical flask containing 5 ml dimethylformamide. 2,2'-Bipyridyl (350 mg) was added to it and the reaction mixture was heated while stirring. The colour of the solution slowly changed to pink-violet and a white solid settled at the bottom, which was filtered and to the filtrate methanol (50 ml) was added and kept for overnight cooling. A pink-violet crystalline compound separated out which was filtered, washed with water, methanol, finally with ether and dried over P_2O_5 desiccator.

Anal. Calcd for $Mo_2C_{20}H_{16}N_4Cl_8$: C, 30.51; H, 2.31; N, 7.11; Cl, 35.99%. Found: C, 29.01; H, 1.14; N, 6.25; Cl, 34.20%.

The parent dinuclear anion $[Mo_2Cl_{11}]^{3-}$ can also be synthesized starting from $[Mo(NO)Cl_5]^{2-}$ using tin and hydrochloric acid. The diamagnetism of these complexes is suggestive of their dimeric nature. The analytical figures show the oxidation state of molybdenum in this series as +4. However, the aqueous chemistry of molybdenum in +4 oxidation state is

very complex in nature [122]. Cotton and coworkers [7, 10, 11] have isolated a series of molybdenum-molybdenum multiple bonded chloro complexes by reacting $[Mo_2(OAc)_4]$ with hydrochloric acid at 0°C and at room temperature. At elevated temperatures, trivalent molybdenum complexes are formed. Hence in the complete denitrosylation processes described above, whether multiply bonded dimolybdenum unit was formed as an intermediate was not known. As a check, $[Mo_2(OAc)_4]$ was allowed to react in concentrated hydrochloric acid containing $SnCl_2$. Addition of NH_4Cl and filtering the reaction mixture from the precipitated $[NH_4]_2[SnCl_6]$ and $[NH_4]_2[SnCl_4]$ in cold and keeping the filtrate for two days, resulted in the separation of the yellow crystalline compound having composition $[NH_4]_3[Mo_2Cl_{11}]$. Interestingly, when the same reaction was carried out in the presence of $NH_2OH.HCl$, $[NH_4]_3[MoCl_6]$ was formed instead. The above reactions with $[Mo_2(OAc)_4]$ suggest that no quadruply or triply bonded dimolybdenum unit is isolable under the reaction conditions used in the denitrosylation reactions.

Nitrosylruthenium complexes like $[Ru(NO)Cl_5]^{2-}$ react with $SnCl_2/HCl$ or $HCHO/OH^-$ to generate dimeric nitrido complex of ruthenium in +4 oxidation state [123]. As $K_4[Mo(NO)(CN)_5]$ on reacting with hydrochloric acid changes to chloronitrosyl-molybdenum complexes [48]. We tried to see the behaviour of nitrosylmolybdenum group towards $SnCl_2$ in hydrochloric acid. Formation of a monomeric $[MoCl_6]^{3-}$ shows that the reaction may

not be proceeding in the same way as observed for ruthenium analog. However, nitrido complexes of molybdenum are known and they are isolable and stable only in aprotic media [124]. Essentially, in these complexes, nitrido group is bound to one molybdenum with the exception of $[MoNCl_3]_4$ [125]. It may be possible that the formation of $[MoCl_6]^{3-}$ may go via an intermediate nitrido complex which _in situ_ may hydrolyze to give ammonia. As a check, a test of $[NH_4]^+$ ion was undertaken after refluxing $K_4[Mo(NO)(CN)_5]$ with $SnCl_2/HCl$. The reaction mixture does not contain any hydroxylamine as confirmed by making a portion of the solution alkaline and performing the Griess's test. It is classically known that 'NO$^+$' can be reduced by $SnCl_2$ in hydrochloric acid to produce hydroxylamine. The negative Greiss's test also suggests that there is no free 'NO$^+$' in the reaction mixture. The reaction may thus proceed via a coordinated nitrido group which immediately hydrolyzes to produce ammonia.

2.6 Disproportionation Reaction of $Cs_2[Mo(NO)Cl_5]$

$Cs_2[Mo(NO)Cl_5]$ (570 mg) was taken in dilute hydrochloric acid (50 ml) and refluxed for about 90 minutes. The solution changed from red brown to green in colour. The volume of the solution was reduced to 5 ml and cooled to room temperature. A green substance was separated. Acetone-HCl (10 ml : 1 ml) -

soluble portion of the compound was extracted and evaporated in vacuo over NaOH. The green crystalline substance thus obtained was analysed and characterized as $Cs_2[Mo(NO)_2Cl_4]$; yield, 75 mg.

Reaction of $Cs_2[Mo(NO)Cl_5]$ with Hydroxylamine

A mixture of $Cs_2[Mo(NO)Cl_5]$ (570 mg) and hydroxylamine hydrochloride (100 mg) was taken in 50 ml of dilute hydrochloric acid and refluxed for about 45 minutes. The solution changed from red-brown to green in colour. The volume of the solution was reduced to 5 ml and cooled to room temperature whereby green crystals separated. Acetone-HCl (20 ml: 2 ml) soluble portion of the green substance was extracted and evaporated in vacuo over KOH; yield 250 mg. The green crystalline compound obtained was analysed and characterized as $Cs_2[Mo(NO)_2Cl_4]$.

The hexacoordinated $Cs_2[Mo(NO)Cl_5]$ is a stable compound as reported earlier. Interestingly, this compound slowly dissolves in dilute hydrochloric acid to give a reddish-brown solution and on increasing the acid concentration, the colour changes to green and an insoluble red-orange $Cs_2[Mo(NO)Cl_5]$ reprecipitates. The colour of the resultant solution still remains green which on careful evaporation gives a mixture of $Cs_2[Mo(NO)_2Cl_4]$ and $Cs_2[MoOCl_5]$. This disproportionation reaction can be represented as:

$$\{Mo(NO)\}^4 \longrightarrow \{Mo(NO)_2\}^6 + \{Mo(IV)\}^{d^2}$$
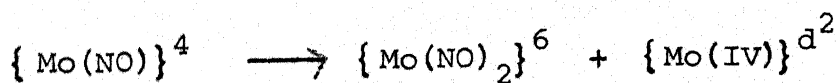
The tetravalent-molybdenum being formed may get oxidised by air into $(MoO)^{3+}$ group. However, for a clean reaction of the above nature, one should expect a 50% yield of the dinitrosyl product. The observed yield is only 10% (vide supra). However, a similar reaction in the presence of hydroxylamine increases the yield to 43%. It is worth mentioning that by taking an excess of hydroxylamine, the yield could be improved. Furthermore in very dilute hydrochloric acid $Cs_2[Mo(NO)_2Cl_4]$ is not appreciably stable for a longer time. The decomposition rate of this complex is faster in presence of air and hence it is presumed that addition of hydroxylamine may just prevent the decomposition. If this be the case, then the 43% yield of $Cs_2[Mo(NO)_2Cl_4]$ does account for the disproportionation scheme. It is further supported by the fact that the bi-product $Cs_2[MoOCl_5]$ does not react with hydroxylamine to give any nitrosyl derivative under the reaction conditions used in this study. Direct dinitrosylation of molybdate for the synthesis of $Cs_2[Mo(NO)_2Cl_4]$ may thus proceed via an intermediate of $Cs_2[Mo(NO)Cl_5]$ (vide supra). It is important to note that NH_2OH nitrosylates $\{MoNO\}^4$ to $\{Mo(NO)\}^6$ but only in the pH range 5.5 - 7.5 (vide infra).

2.7 Bioinorganic Aspect of $\{Mo(NO)\}^4$ Moiety

Molybdenum is the only heavy transition metal that is known to be essential in living systems. The concentration of

molybdenum exceeds over any other transition metal in sea water [126]. Recently Egami and coworkers [109] have studied extensively the possible role of MoO_4^{2-} in catalysing the formation of several aminoacids from HCHO and NH_2OH (relevant starting materials according to the investigations of Oró [127]) in a 'modified sea medium'. Substances dissolved in the earth's primeval sea are regarded as the initial materials for the development of life [128]. The role of molybdate as the environmental catalyst has been suggested by Egami and coworkers with the proposed mechanism for such reactions as the formation of HCN as the precursor.

$$NH_2OH + HCHO \longrightarrow CH_2-NOH + H_2O$$

$$CH_2-NOH \longrightarrow HCN + H_2O$$
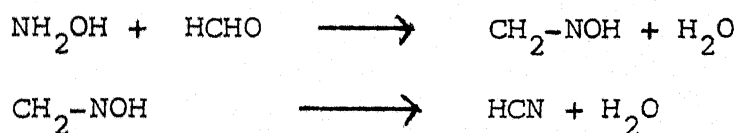
Two important questions arise from the above dehydration processes: (i) Would a stepwise elimination of water take place in an aqueous medium? (ii) Could an hexavalent molybdenum have existed in prebiotic condition which was of non-oxidising nature?

It is possible that a reduced molybdenum species is involved in the catalytic activity and is acting as a metal template condenser which may allow successive dehydration processes even in an aqueous medium. For verification of the above statement the following experiments were carried out.

(a) HCHO being a reducing agent may reduce a molybdate to its lower oxidation states. The reactions between molybdate

and formaldehyde were done under different pH conditions and it was found that HCHO could reduce $MoO_4{}^{2-}$ (VI) to Mo(V). One may conclude that HCHO has neither a redox nor any complex chemistry with $MoO_4{}^{2-}$ in aqueous medium within the pH range of biological interest.

(b) Recent investigations [140] demonstrate that complexes with $\{Mo(NO)\}^4$ configuration are formed in neutral or slightly acidic molybdate solutions in the presence of hydroxylamido- and other ligands. Generally two groups are obtained in such reactions, that is $\{Mo(NO)\}^4$ and $\{Mo(NO)(NH_2O)\}^4$. One has to see whether $\{Mo(NO)\}^4$ or $\{Mo(NO)(NH_2O)\}^4$ can react with formaldehyde to generate HCN. For this, a series of experiments with change in the molar ratio between molybdate and hydroxylamine were done and the catalytic activity of this reaction mixture was monitored by their ability to generate HCN on reaction with dilute formaldehyde. Identification of HCN was done by employing the method as described by Schilt [129]. Preparation of different solutions were done in the following manner.

$Na_2MoO_4 \cdot 2H_2O$ (363 mg) was dissolved in 0.5 M NaCl solution and $NH_2OH \cdot HCl$ (104.2 mg) was added to it. The pH of the solution was adjusted to 5.5 by adding KOH solution in 0.5 M NaCl and the final volume was made up to 10 ml by adding 0.5 M NaCl solution to give a concentration of $MoO_4{}^{2-}$ (0.15 M) and NH_2OH (0.15 M) in (1(a):1) ratio. For others, $NH_2OH \cdot HCl$ was added: 208.4 mg for (1(a):2); 312.6 mg for (1(a):3) and 521 mg for

(1(a):5). The final concentration of $MoO_4{}^{2-}$ and NH_2OH in the test solutions are 0.15 M: 0.15 M (1:1); 0.15 M: 0.30 M (1:2); 0.15 M: 0.45 M (1:3); 0.15 M:0.75 M (1:5) respectively. For the less soluble $Cs_2[Mo(NO)Cl_5]$, 57 mg of this was taken against 7.0 mg of $NH_2OH.HCl$ to get (1(b):1) in 0.01 M concentration ratio. The results are set out in the Table 2.2.

When molybdate-hydroxylamine ratio is upto 1:3, the HCN formation is negative. (The test remains positive at room temperature after $1\frac{1}{2}$ hours when the ratio is 1:3). The known chemistry of the molybdate(VI)-hydroxylamine interactions suggests that in generating $\{Mo(NO)\}^4$ moiety, this is the optimum stoichiometric ratio of these reactants [130]. When the ratio of hydroxylamine is increased the test is positive.

This suggests that the $\{Mo(NO)\}^4$ configuration can catalyse the condensation reactions of NH_2OH and $HCHO$ to generate HCN. To substantiate this, the catalytic activity of pure $[Mo(NO)Cl_5]^{2-}$ was tested and found to be positive. Interestingly, the lack of catalytic activity of tungstate supports this view as no nitrosyltungsten chemistry is known by the interaction of tungstate(VI) and hydroxylamine under similar conditions. However, chromium lacks the catalytic activity and it can readily form a $\{Cr(NO)\}^5$ moiety [47] suggesting something more about the $\{Mo(NO)\}^4$ moiety. This can be viewed as follows. The $\{Mo(NO)\}^4$ moiety is able to expand its octahedral coordination to hepta-coordination by chelation of

Table 2.2.   Catalytic Activity of $[MoO_4]^{2-}$ or $\{Mo(NO)\}^4$ moiety to generate HCN with HCHO in the presence of Varying Amounts of Hydroxylamine at Different Conditions in 0.5 M NaCl Aqueous Medium, pH = 5.5.

| Ratio between $[MoO_4]^{2-}$ (a) or $[Mo(NO)Cl_5]^{2-}$ (b) with hydroxylamine (test) solution	Temp. of the medium(°C)	Time of addition[ø] of HCHO into the test solution (in minutes)	Results[≠] HCN test
1(a):1	20	0	-ve
		90	-ve
	60	0	-ve
		90	-ve
1(a):2	20	0	-ve
		90	-ve
	60	0	-ve
		90	-ve
1(a):3	20	0	trace
		90	+ve
	60	0	trace
		90	-ve
1(a):5	20	0	+ve
		90	+ve
	60	0	+ve
		90	+ve
1(b):1	20	0	+ve
		90	+ve
	60	0	+ve
		90	+ve
1(a):0	20	0	-
		90	-

ø A ten-fold dilute solution of formaldehyde e.g., 0.015 M for (a) and 0.001 M for (b) were used in equal volume to the test solution.

≠ Trace meant a faint colour in $CHCl_3$ alike to a blank run with NH_2OH and HCHO employing the method.

hydroxylamido (-I and -II) group resulting from the stepwise deprotonation of hydroxylamine. As described earlier in this chapter, the preparation of $[Mo(NO)(NH_2O)(NCS)_4]^{2-}$ requires a hydroxylamine-molybdate ratio of 4:1. As a matter of fact, the synthesis of all $\{Mo(NO)_2\}^6$ derivatives requires this ratio in order to achieve a maximum yield. All these reactions thus indicate the formation of $\{Mo(NO)\}^4$ moiety first, which may be further coordinated by hydroxylamido group to give $\{Mo(NO)(NH_2O)\}^4$ moiety. A complex having the later group that is $[Mo(NO)(NH_2O)(NCS)_4]^{2-}$ would be more stable compared to the complex containing only $\{Mo(NO)\}^4$ moiety, especially a complex like $[Mo(NO)Cl_5]^{2-}$ because of its 18-electron configuration.

The hepta-coordinated hydroxylamido group - chelated compound was prepared at pH 5.5 and its structure has been established recently [131]. Nitrosylchromium complexes have only a hexa-coordination and there is no evidence till date that hydroxylamido group may be chelated with this moiety to give a hepta-coordinated species. From effective atomic number rule, if such compounds are formed, they would be having a 19-electron configuration and would not be stable. So an $\{Mo(NO)\}^4$ group can enhance its coordination number by chelation with a hydroxylamido group whereby its stability increases. The availability of two different coordination numbers and stability of a hydroxylamido group configuration make this system ideal for its catalytic activity. The mechanistic view

of the HCN generating cycle is as follows:
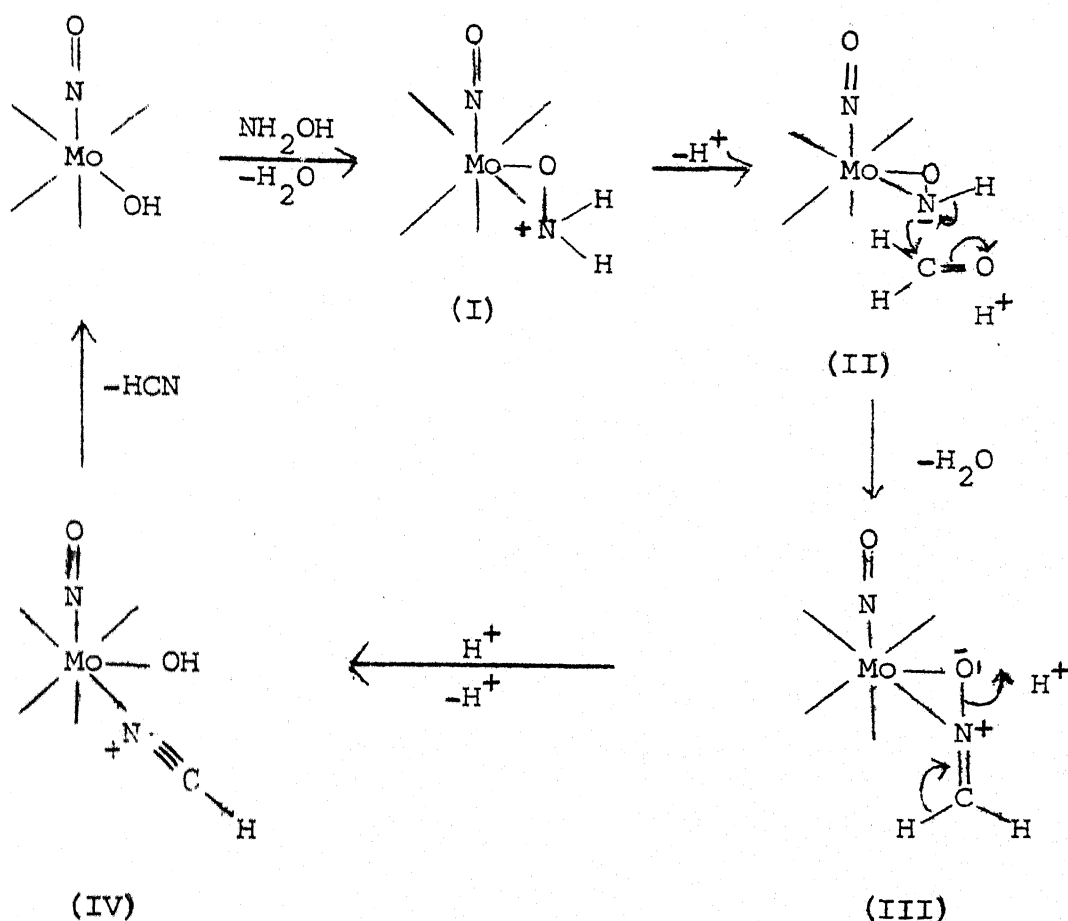
Compounds containing groups (I) and (II) have already been characterised by W ghardt and coworkers [103]. Compounds containing group (III) as coordinated oximato ligand have been structurally characterized recently [108]. Furthermore, through our experiments with the formation of 'dtc' complexes of $\{Mo(NO)\}^4$, we have found that acetone is a must to carry out this reaction to prevent dinitrosylation. For the characterisation of the species containing group (IV), we were unable to isolate any product. This is nothing surprising as there

is no bidentate ligand in this configuration which can stabilize the moiety. HCN attachment to the central molybdenum through nitrogen is going to be very weak, once the ring opening from (III) to (IV) takes place. The elimination of HCN is instantaneous whereby an unstable hexa-coordinated compound of $\{Mo(NO)\}^4$ configuration generated, which by its reactivity immediately reacts with a second molecule of hydroxylamine whereby a continuous cycle of HCN generation may be achieved. Reacting $[Mo(NO)Cl_5]^{2-}$ with hydroxylamine followed by acetaldehyde and monitoring the formation of acetonitrile by infrared shows the appearance of an absorption at 2240 cm^{-1} and no other absorption is noticed in this range which suggests that as soon as the ring opening starts, CH_3CN is detached from the metal centre.

RESULTS AND DISCUSSION

3.1 Structural Aspects of the Prepared Complexes

IR Spectra

IR spectra in the range 4000-200 cm^{-1} and 4000-400 cm^{-1}
were recorded on Perkin Elmer model 580 and 377 Infrared
Grating Spectrometers respectively. Samples were prepared as
KBr or CsI pellets. Far IR spectra were recorded with polytech
FIR-30 Fourier IR and Hitachi FIS-1 Spectrometers in the range
600-100 cm^{-1} and 400-30 cm^{-1} respectively.

Magnetic Susceptibility Measurements

These measurements were made using a Guoy balance at
room temperature using a magnetic field of 8500 Gauss. Mercury
tetrathiocyanatocobaltate(II) was used as a calibrant.

ESR Spectra

ESR spectra of the complexes were recorded on a Varian E-4
ESR instrument working at X-band.

NMR Spectra

^{1}H-NMR spectra of the complexes were recorded on a Varian (60-MHz) instrument, Varian HA-100, Varian XL-100 FT NMR Spectrometer or JEOL FX-100 FT NMR Spectrometer.

^{13}C NMR spectra of the complexes were recorded on a Brucker FT NMR Spectrometer working at 67.89 MHz.

X-Ray Photoelectron Spectrum

The spectrum of $Cs_2[Mo(NO)_2Cl_4]$ was recorded on ESCA-3 type spectrometer of Vacuum Generators using Al-K$_\alpha$ radiation (1846.6 eV) at a pressure between 5×10^{-9} to 1×10^{-8} torr. The binding energies reported were standardised using C(1s) binding energy of 285.0 eV. The spectrum was recorded at ambient temperature.

Infrared Spectra of the Complexes

Complexes Containing $\{Mo(NO)_2\}^6$ Moiety

The recorded IR spectra of these complexes are reproduced in Fig. 3.1 to 3.8. The important absorptions are presented in Table 3.1. The appearance of two very strong bands in the range 1785-1740 and 1670-1620 cm^{-1} suggests that the two nitrosyl groups are attached to the metal in cis - fashion. This is in accordance to the expectation of Feltham and Enemark [133] based on molecular orbital energy level diagram. The characterization of $\nu_{(Mo-N)}$ and $\delta_{(Mo-N-O)}$ is based on their
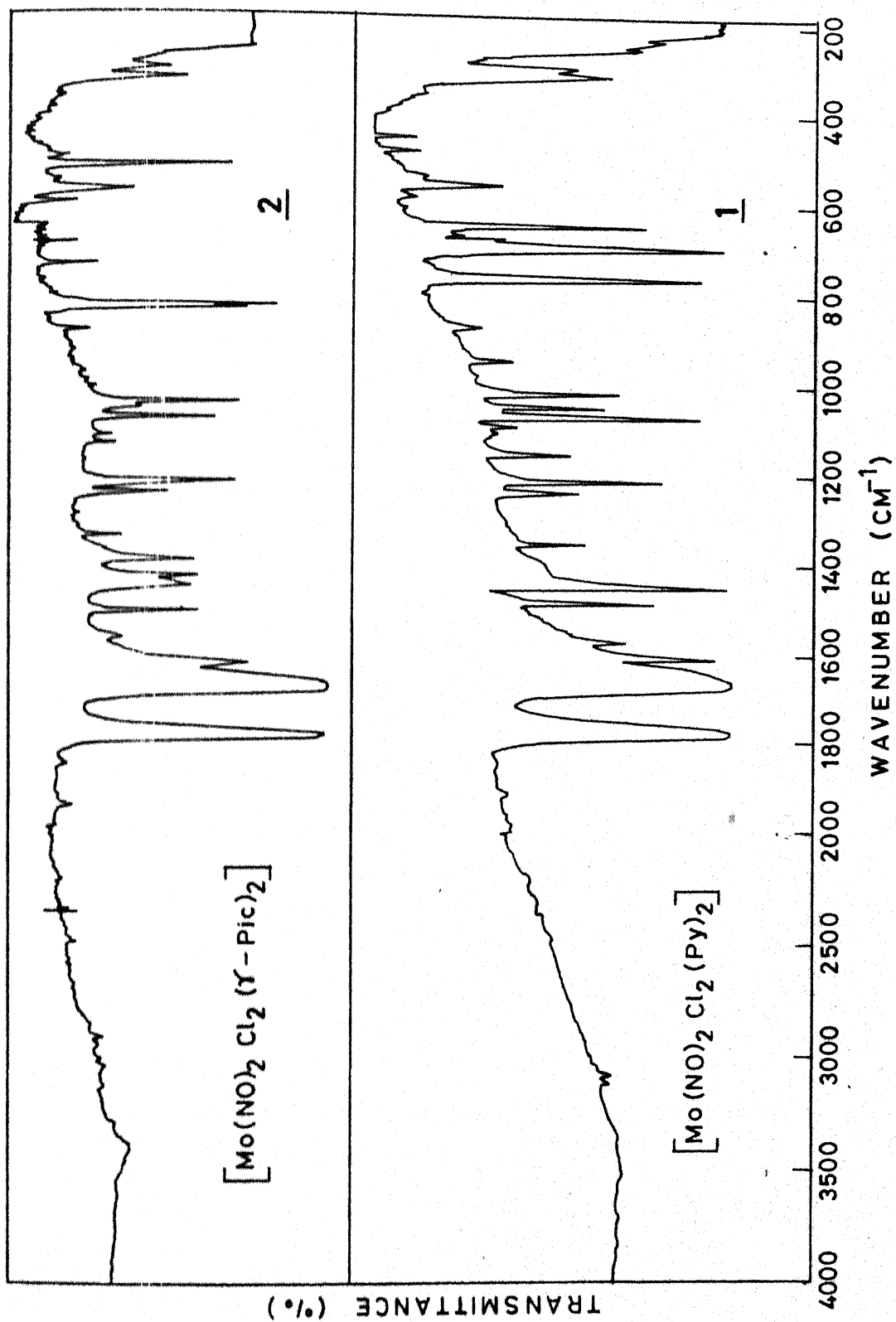
FIG. 3.1 IR SPECTRA OF 1 & 2.
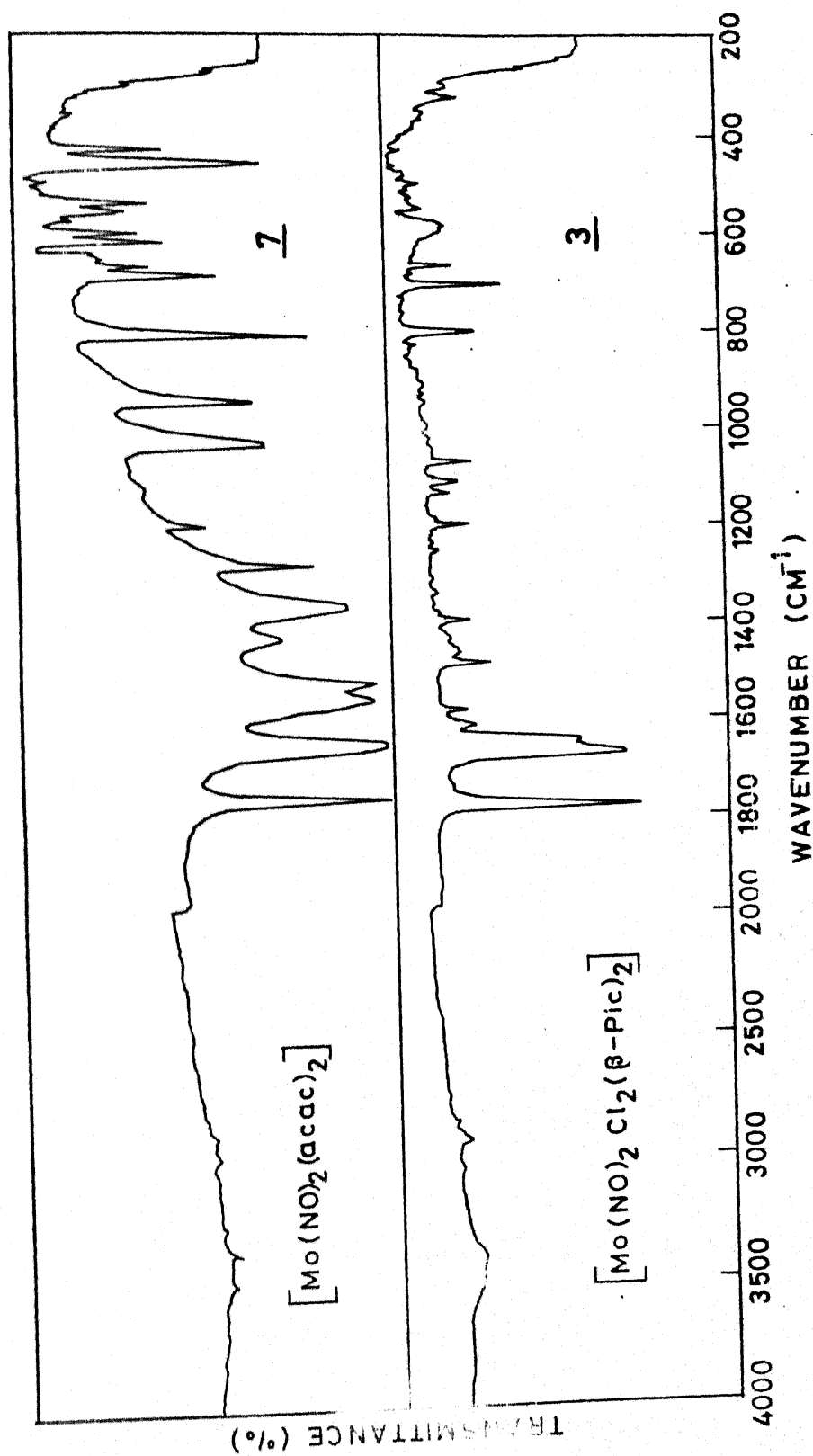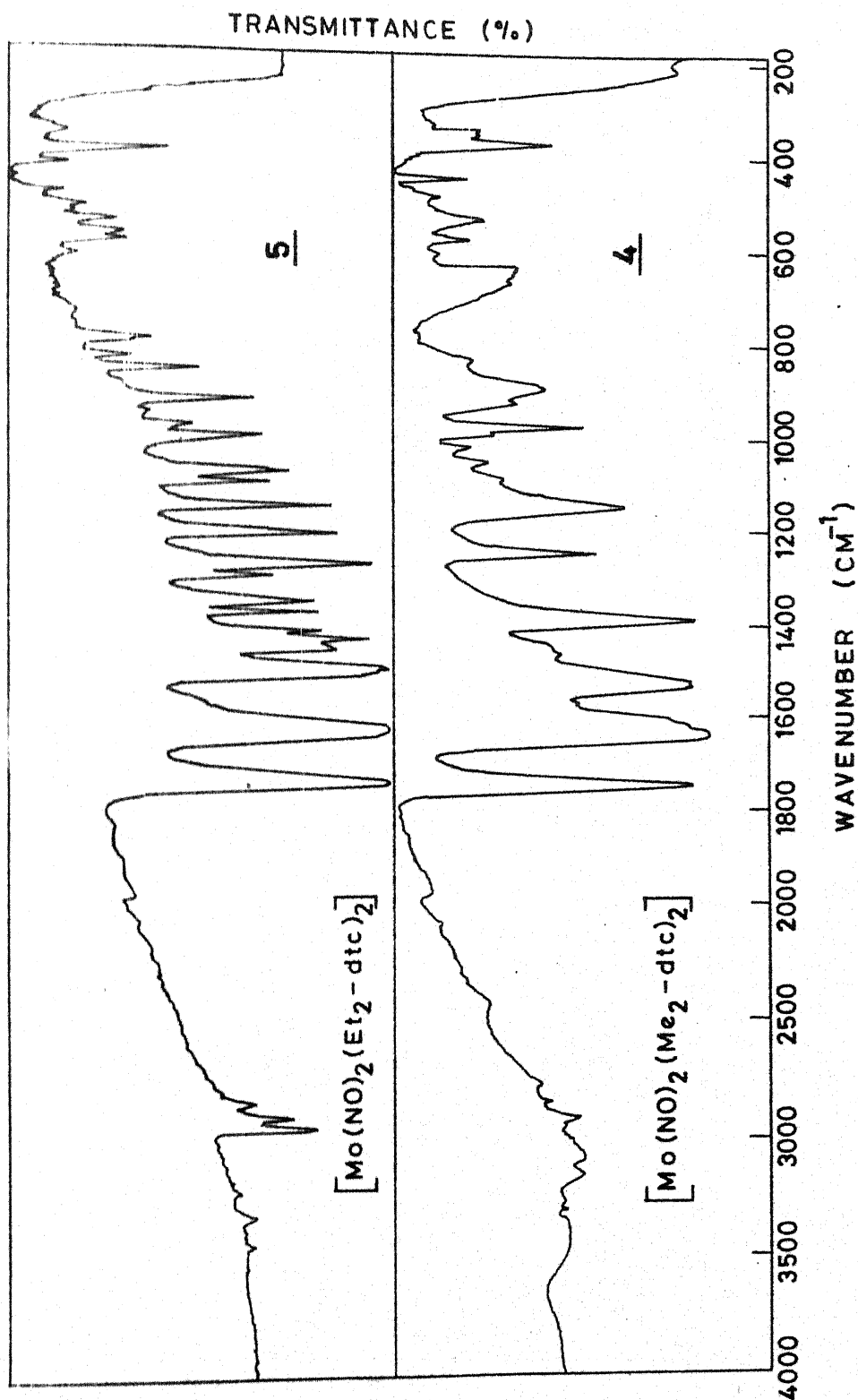
FIG. 3.2   IR   SPECTRA   OF   3 & 2 .
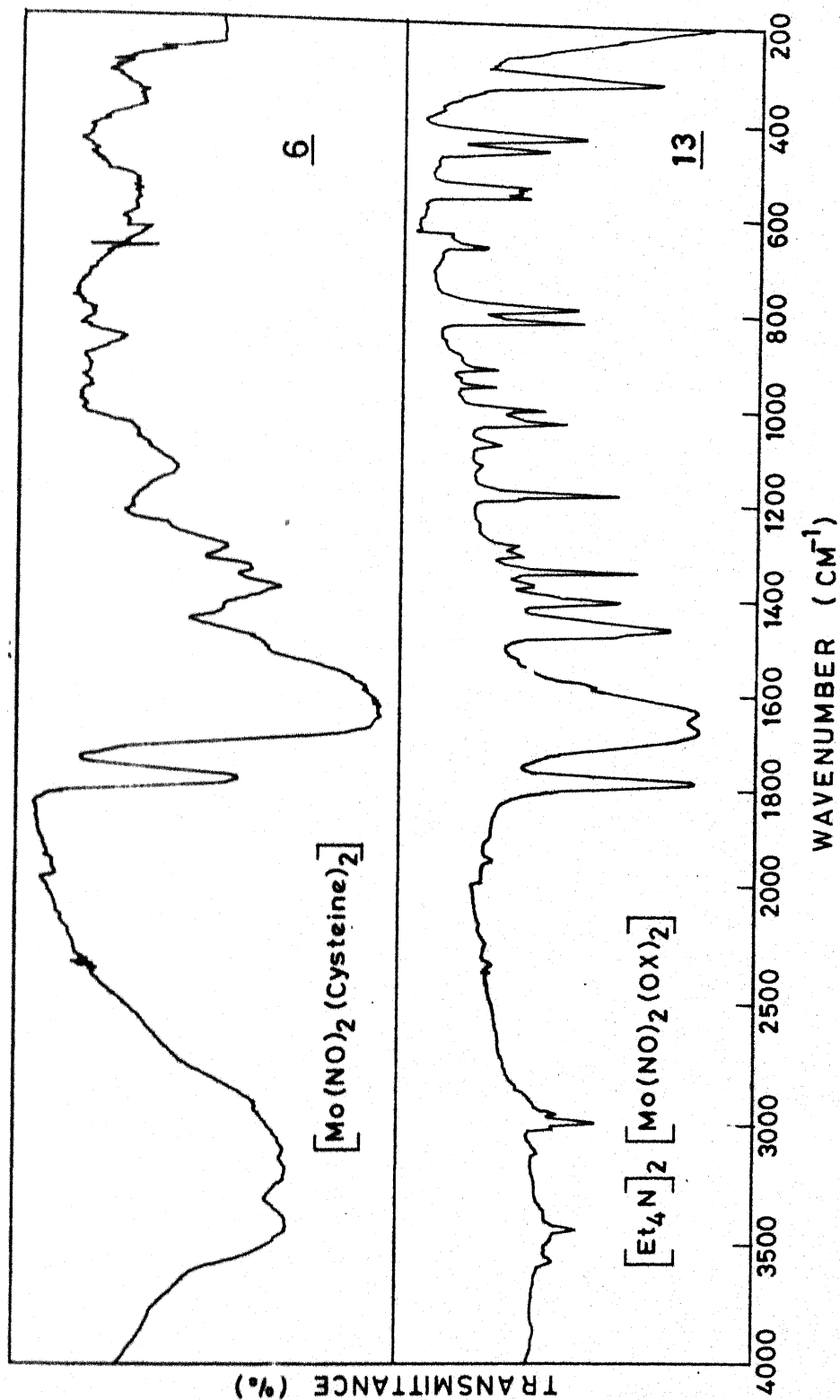
76

77

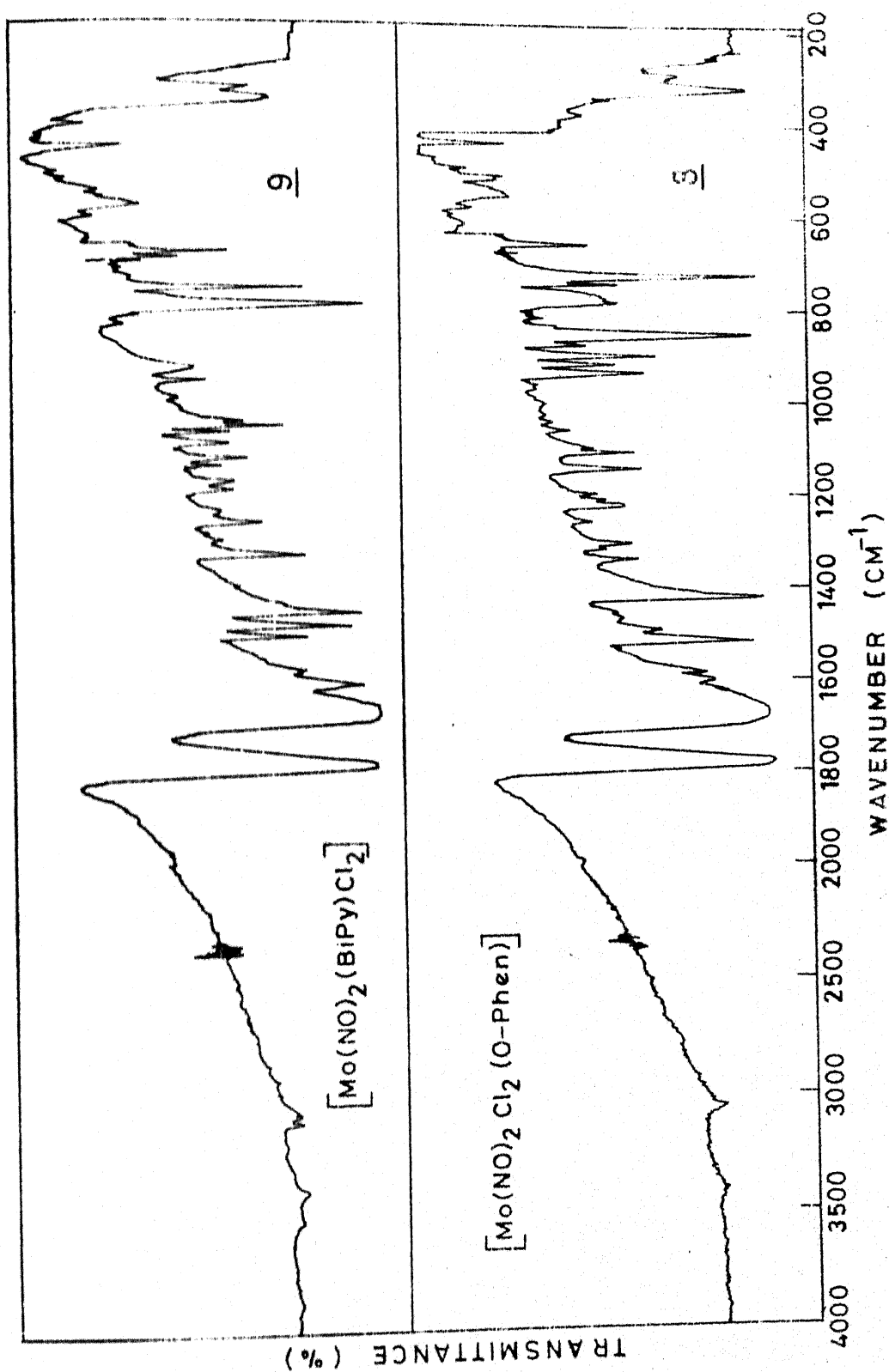FIG. 3.3 IR SPECTRA OF 4 & 5.

FIG. 3.4 IR SPECTRA OF 6 & 13.

FIG. 3.5 IR SPECTRA OF 8 & 9
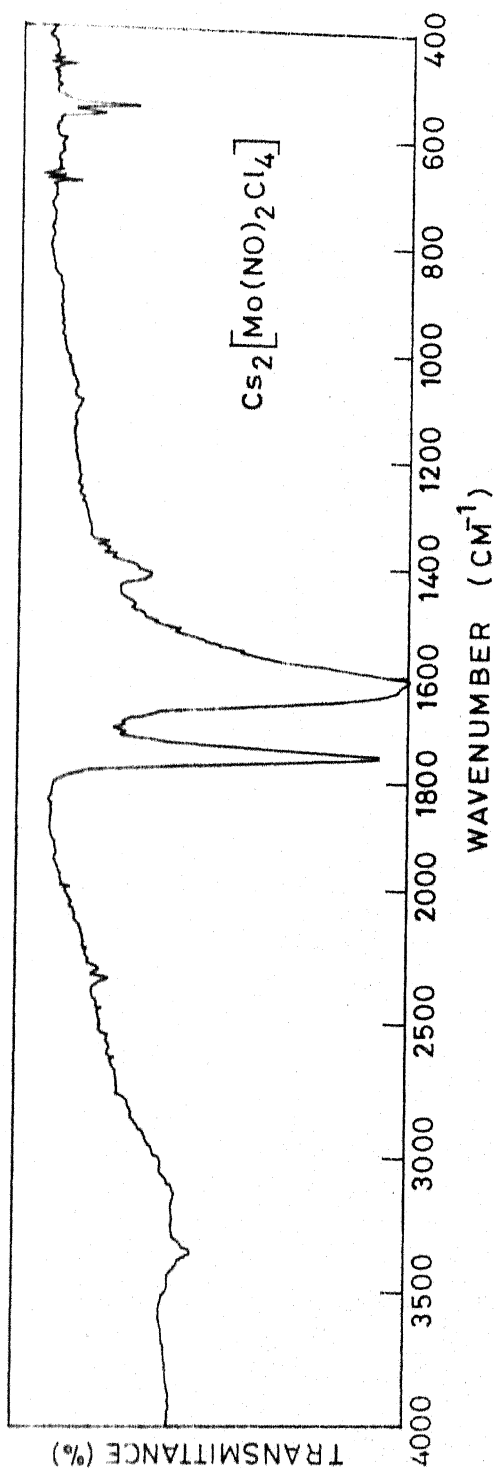
$[Mo(NO)_2(BiPy)Cl_2]$

$[Mo(NO)_2 Cl_2 (O-Phen)]$

FIG. 3.6a IR SPECTRUM OF 10.
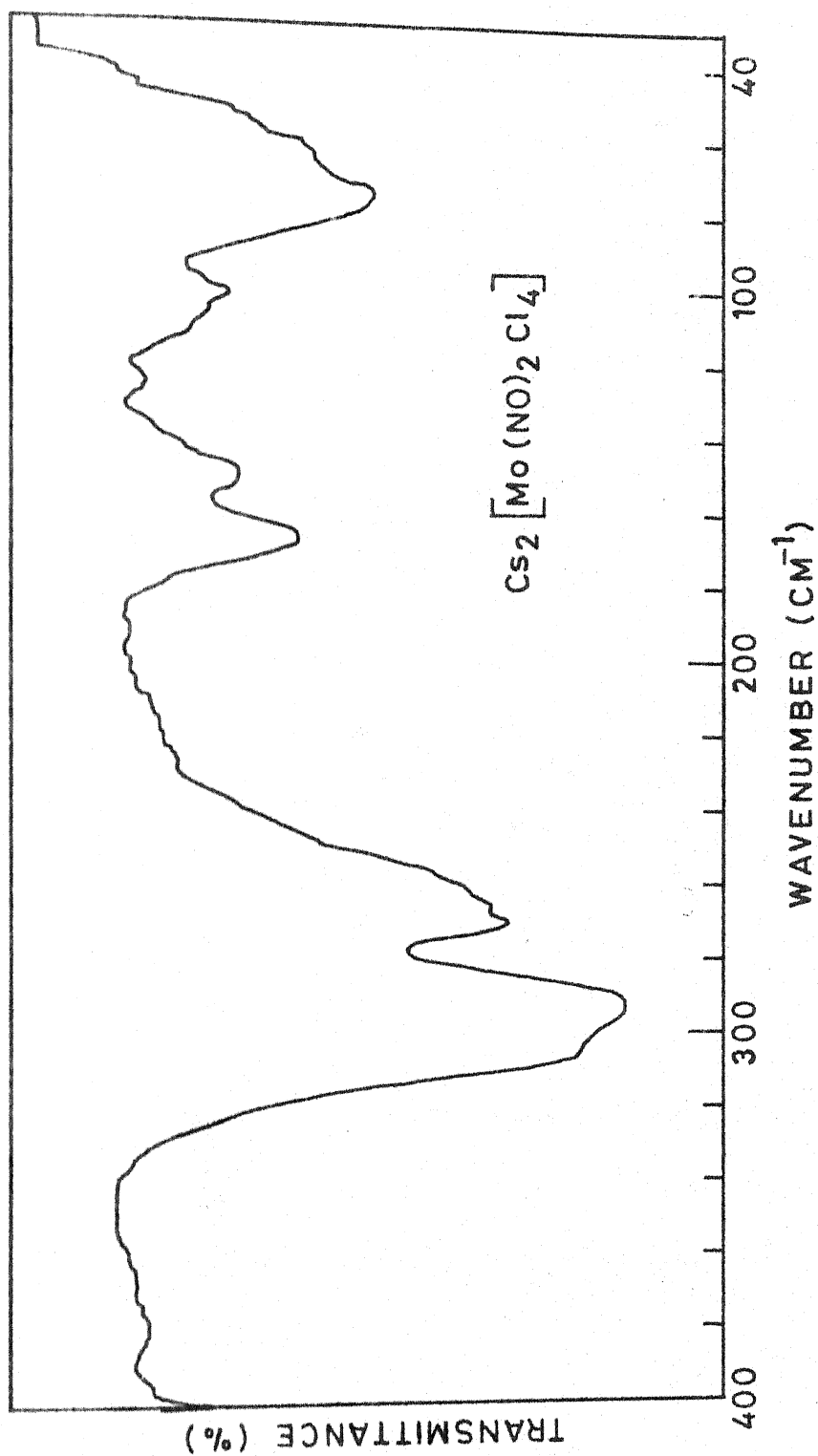
FIG. 3.6b Far - IR SPECTRUM OF 10.

$Cs_2[Mo(NO)_2Cl_4]$

WAVENUMBER (CM^{-1})

TRANSMITTANCE (%)

$[Et_4N]_2[Mo(NO)_2(CN)_4]$

WAVENUMBER (CM^{-1})

TRANSMITTANCE (%)
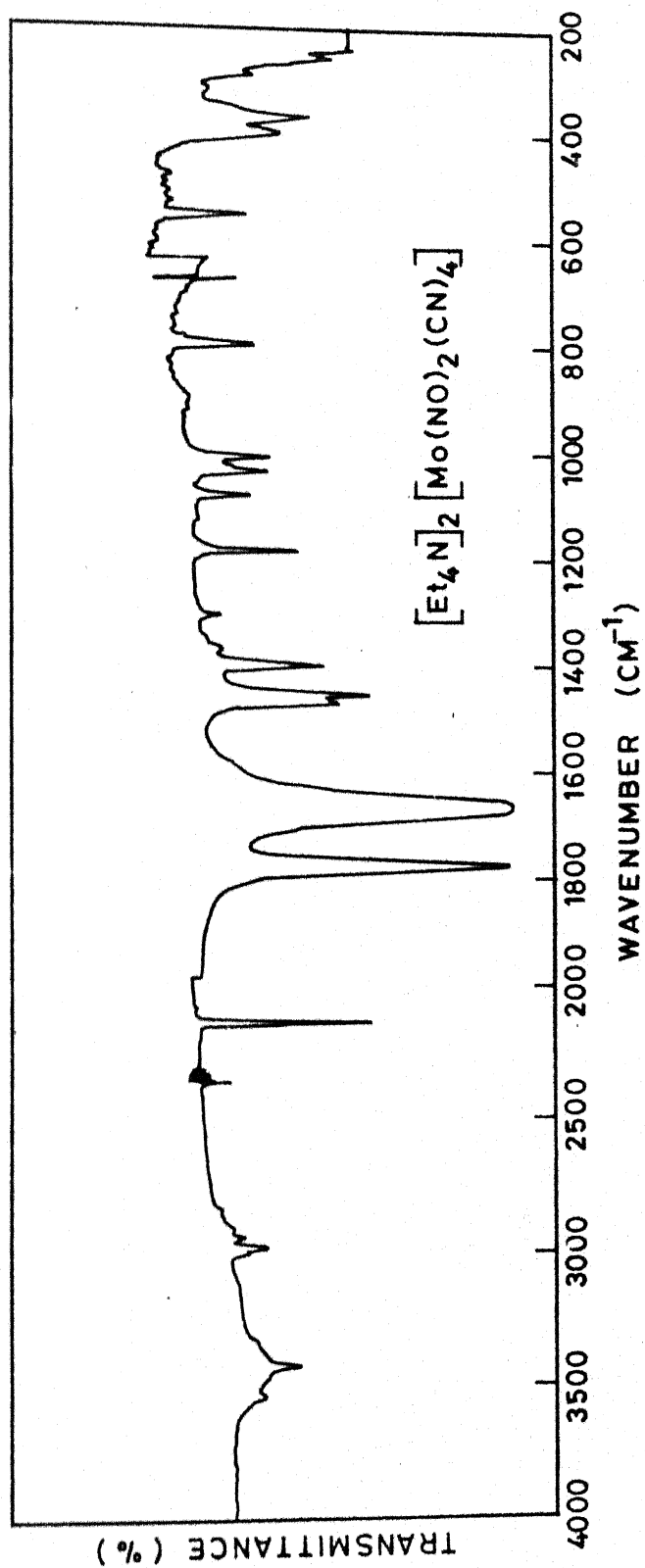
FIG. 3.7 IR SPECTRUM OF 11.

FIG. 3.8 IR SPECTRUM OF 12.

$[Ph_4 P]_2 [Mo(NO)_2 (NCS)_4]$

WAVENUMBER (CM^{-1})

TRANSMITTANCE (%)

Table 3.1
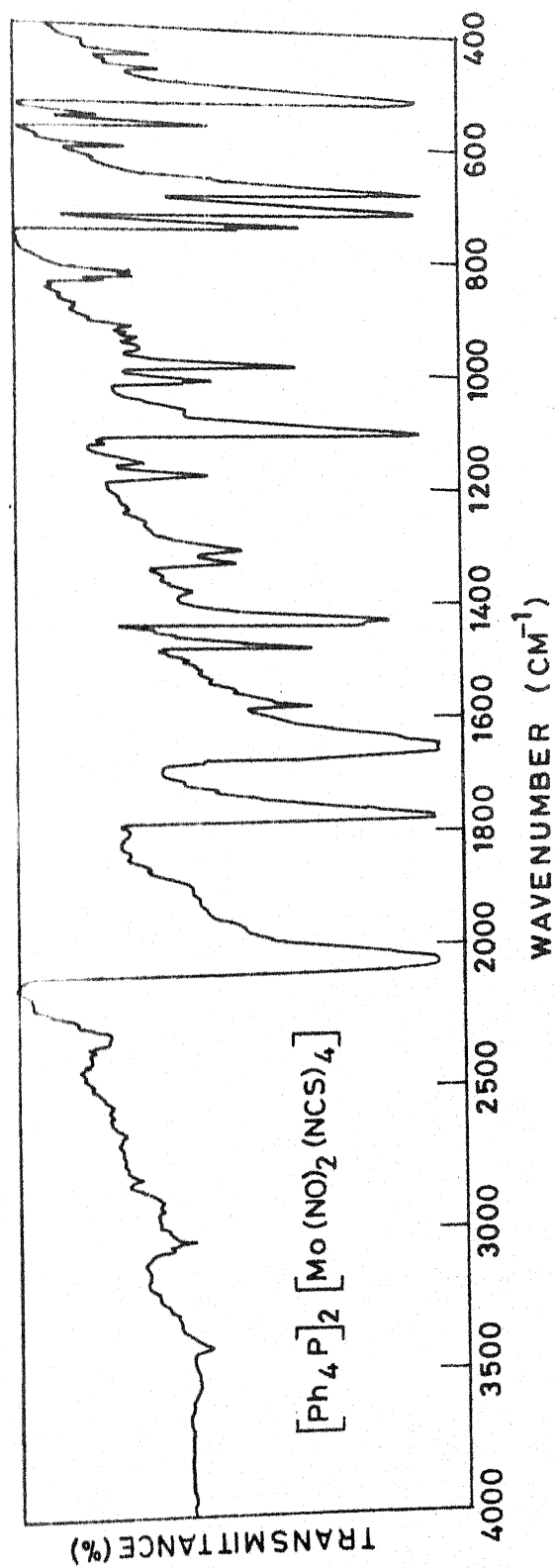
| Sl. No.	Compound	ν_{NO} s' (cm^{-1})	ν(Mo–N)/δ(Mo–N–O) (cm^{-1})	Other important vibrations (cm^{-1})
1.	[Mo(NO)$_2$Cl$_2$(Py)$_2$]	1780(vs), 1670(vs)	580(w), 555(m), 575(w)	312, 280 ν(Mo–Cl)
2.	[Mo(NO)$_2$Cl$_2$(γ-pic)$_2$]	1780(vs), 1760(vs)	580(m), 555(m), 475(w)	310, 280 ν(Mo–Cl)
3.	[Mo(NO)$_2$Cl$_2$(β-pic)$_2$]	1775(vs), 1670(vs)	570(w), 545(w), 485(w)	310, 285 ν(Mo–Cl)
4.	[Mo(NO)$_2$Cl$_2$(o-phen)]	1790(vs), 1680(vs)	570(w), 545(m), 485(w)	318, 285 ν(Mo–Cl)
5.	[Mo(NO)$_2$(bipy)Cl$_2$]	1785(vs), 1675(vs)	565(w), 545(m), 485(w)	320, 295 ν(Mo–Cl)
6.	[Mo(NO)$_2$(acac)$_2$]	1770(vs), 1655(vs)	562(w), 545(m), 475(m)	440, 415 ν(Mo–O)
7.	[Mo(NO)$_2$(Me$_2$-dtc)$_2$]	1760(vs), 1655(vs)	572(m), 530(m), 480(w)	370, 350 ν(Mo–S)
8.	[Mo(NO)$_2$(Et$_2$-dtc)$_2$]	1755(vs), 1645(vs)	570(m), 528(m), 460(w)	375, 330 ν(Mo–S)
9.	[Mo(NO)$_2$(cysteine)$_2$]	1795(vs), 1650(br)	–	–
10.	Cs$_2$[Mo(NO)$_2$Cl$_4$]	1765(vs), 1620(vs)	560(m), 545(m), 472(w)	295, 270, ν(Mo–Cl)
11.	[Et$_4$N]$_2$[Mo(NO)$_2$(CN)$_4$]	1785(vs), 1775(vs)	550(m), 470(w)	2140(vs) ν(C≡N)
12.	[PPh$_4$]$_2$[Mo(NO)$_2$(NCS)$_4$]	1775(vs), 1655(vs)	570(m), 560(w), 475(w)	2060(vs) ν(C≡N)
13.	[Et$_4$N]$_2$[Mo(NO)$_2$(ox)$_2$]	1785(vs), 1630(vs)	565(m), 552(m)	465, 438 ν(Mo–O)

br, broad; m, medium; vs, very sharp; w, weak.

low intensity. It is now established that the position of ν_{N-O} in no way reflects the mode of attachment of the nitrosyl group to the metal. Interestingly, even with a linear mode of attachment M-N-O as observed in X-ray structural investigations, the highest ν_{NO} is observed for $Na_2[Fe(NO)(CN)_5]$ at 1944 cm^{-1} and the lowest has been recorded at 1455 cm^{-1} for $K_4[Mo(NO)(CN)_5]$. However, several factors affect this ν_{NO} and its correlation with the mode of attachment is meaningless [133]. Meaningful correlation can be made in this regard by locating the associated $\nu_{(M-N)}$ and $\delta_{(M-N-O)}$. An unequivocal assignment of these vibrations require ^{15}N substitution as well as Raman polarization data. Miki, using a linear 3-body model, has assigned the higher wave number band to $\nu_{(M-N)}$ and the lower one to M-N-O bending vibration [132]. However, this model would not be applicable in the present case as the two nitrosyl groups are cis to each other. Using a large number of derivatives with varying co-ligands of this $\{Mo(NO)_2\}^6$ moiety, one can atleast locate the appearance of low frequency vibrations responsible for $\nu_{(Mo-N)}$ and $\delta_{(M-N-O)}$. These vibrations along with $\nu_{NO}s'$ are presented in the Table 3.1. An interesting correlation may be obtained from this series $[Mo(NO)_2X_4]^{2-}$ (X = NCS^-, Cl^-, CN^-) regarding the low frequency vibrations responsible for $\nu_{(Mo-N)}$ and $\delta_{(Mo-N-O)}$. Taking the corresponding chloro complex as a reference compound, Mo-Cl vibrations of which do not appear in this region, we find a trend in two weak absorption bands in the region 570-550 cm^{-1} and

475-470 cm^{-1}. The respective position of these bands are: 550, 470 cm^{-1} for the cyano complex, 560, 472 cm^{-1} for the chloro and 570, 475 cm^{-1} for the thiocyanato analog. If we assign tentatively these sets of vibrations originating from Mo-N stretching vibrations, the competitive bonding ability of these three co-ligands can be clearly seen. The order thus emerging is CN > Cl$^-$ > -NCS$^-$. With the series of neutral complexes, there is no appreciable change in the appearance of the ν_{NO} band at the higher frequency. However, the lower frequency ones sometimes appear at a slightly higher frequency range. This shift is dependent on the overall charge of the complex as normally encountered for other coordination compounds. The insensitivity of the ν_{NO} s' to the overall charge of the complex is unexpected. The electronic distribution between Mo, N and O in Mo-N-O is not fully understood.

Feltham and Enemark [133] have proposed that the M-N-O group may be treated as an inseparable inorganic functional group. However, sometimes the ν_{NO} s' are sufficiently sensitive to the nature of cation present. For example, in $Cs_2[Mo(NO)_2Cl_4]$ ν_{NO} s' appear at 1755 and 1620 cm^{-1} whereas in $[PPh_4]_2[Mo(NO)_2Cl_4]$, these streches are at 1720 and 1600 cm^{-1} [134]. By observing the nature of the vibrational peaks due to the presence of other co-ligands, one can distinguish the nature of stereoisomers. Thus, Johnson recorded the appearance of two $\nu_{(Mo-Cl)}$ at 346 and 318 cm^{-1} for the complex

$[Mo(NO)_2Cl_2(PPh_3)_2][134]$. This is suggestive of the presence of one of the following two geometrical isomers.
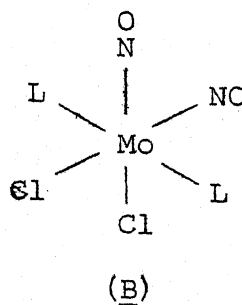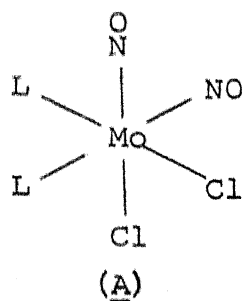

X-ray crystallographic analysis has confirmed the structure (B) where both the phosphines are attached in the trans-position [135]. Previously, we have recorded the far infrared spectrum of $[Mo(NO)_2Cl_2(Py)_2]$ upto 300 cm^{-1} and found the presence of only one $\nu_{(Mo-Cl)}$ at 312 cm^{-1} and on this basis suggested that it was the stereoisomer containing the cis ligand trans-chloro isomer [136]. Complexities due to the presence of two neutral donors in the cis-position arise for this type of compounds while analysing the NMR data (vide infra) and so, Far-IR data of this series of compounds have been obtained down to 200 cm^{-1}. For all the derivatives containing neutral nitrogen donors, two IR stretchings are observed in the range 320-280 cm^{-1}. The appearance of two $\nu_{(Mo-Cl)}$ for these complexes prove that the chloro groups are located cis to each other. For the monodentate pyridine or picoline derivatives, either of the stereoisomers (A) and (B) is possible. However, for the bidentate aromatic diimine derivative only (A)

stereoisomer is possible.

Cysteine derivative of $\{Mo(NO)_2\}^6$ moiety is coordinated through sulphur and nitrogen sites of the cysteine molecule. It is difficult to notice the changes in the $\nu_{(C=O)}$ for the carboxylate group in this complex as it is masked by the strong absorption of ν_{NO} at 1650 cm^{-1}.

Also the presence of the O-H stretches around 3500 cm^{-1} indicates that the carboxylic acid proton is not dissociated from the ligand and it is present as COOH group even in the complex. The free S-H stretch at 2540 cm^{-1} disappeared by the formation of the complex. The non-electrolytic nature of the complex is consistent with the structure given below:
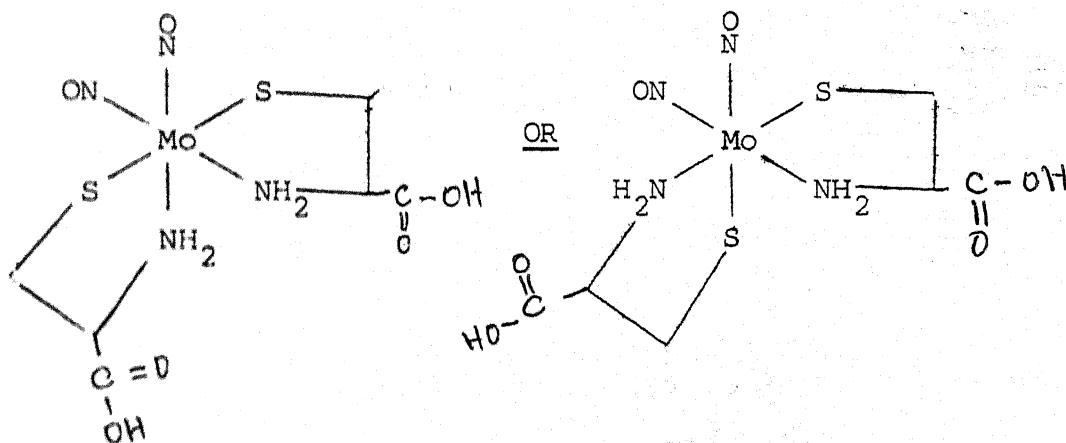
Mononitrosylmolybdenum derivatives

IR spectra of mononitrosylmolybdenum derivatives are reproduced in Figs. 3.9 - 3.13. The important absorptions are
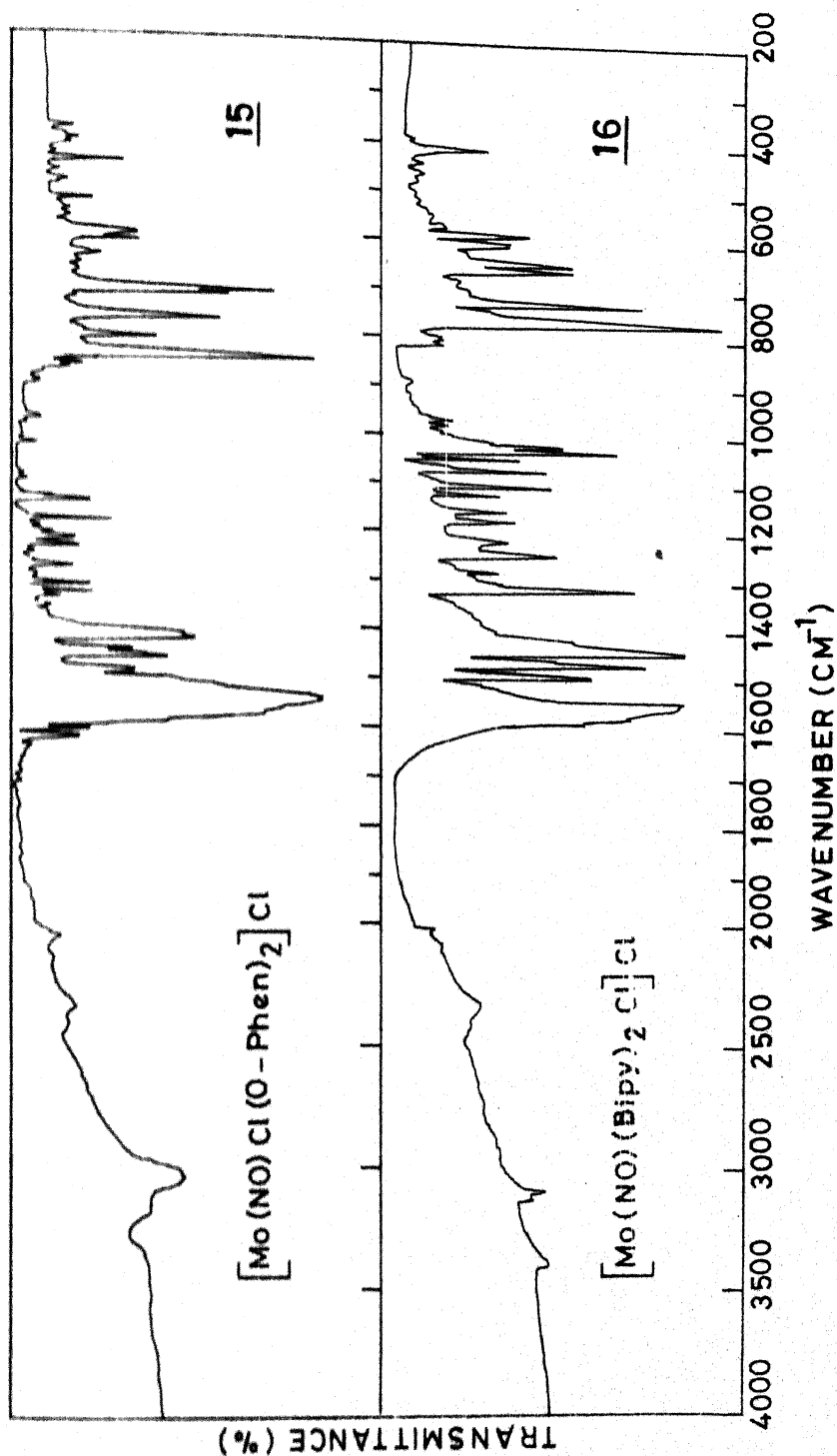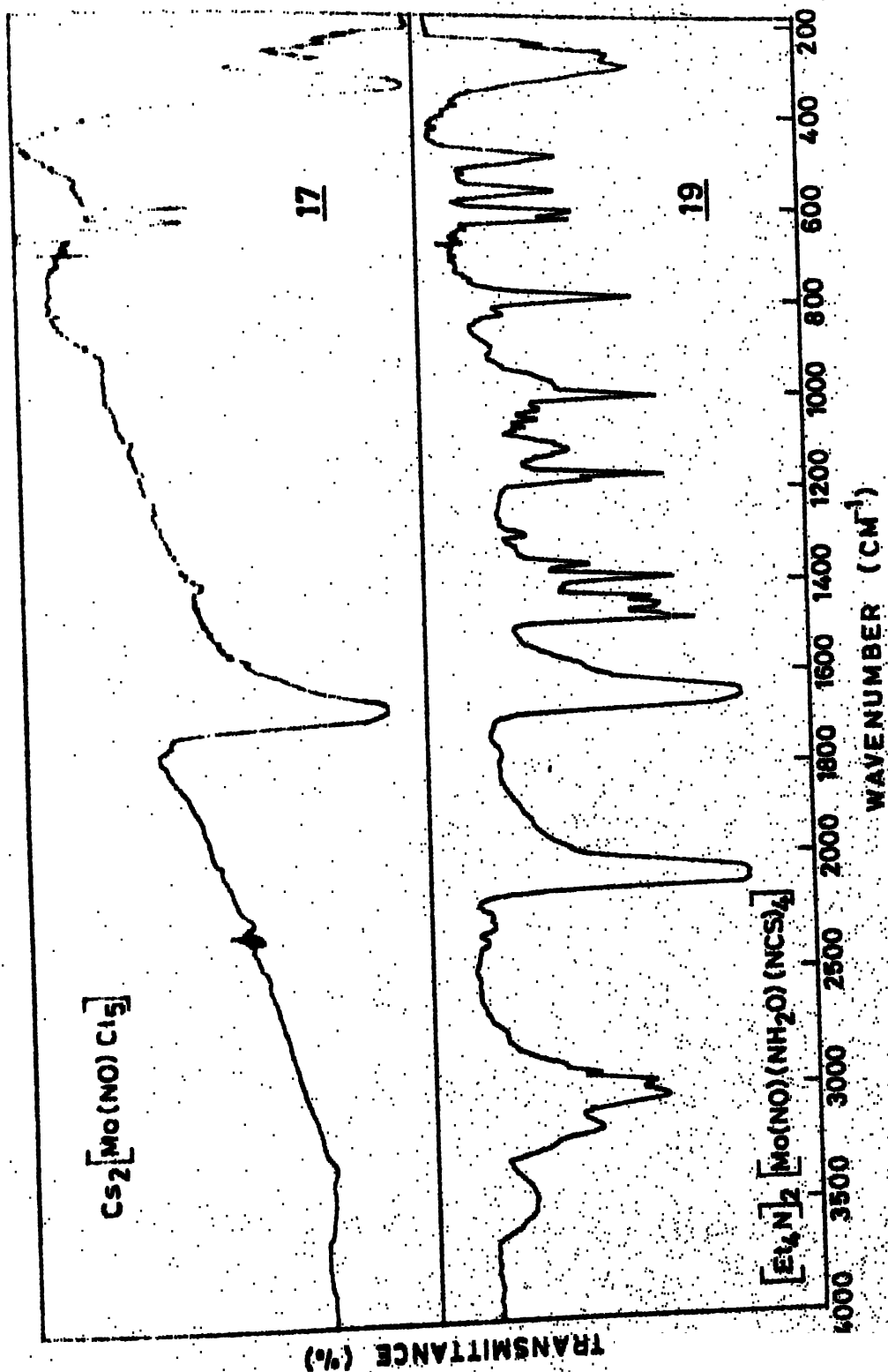
FIG. 3.9 IR SPECTRA OF 15 & 16.
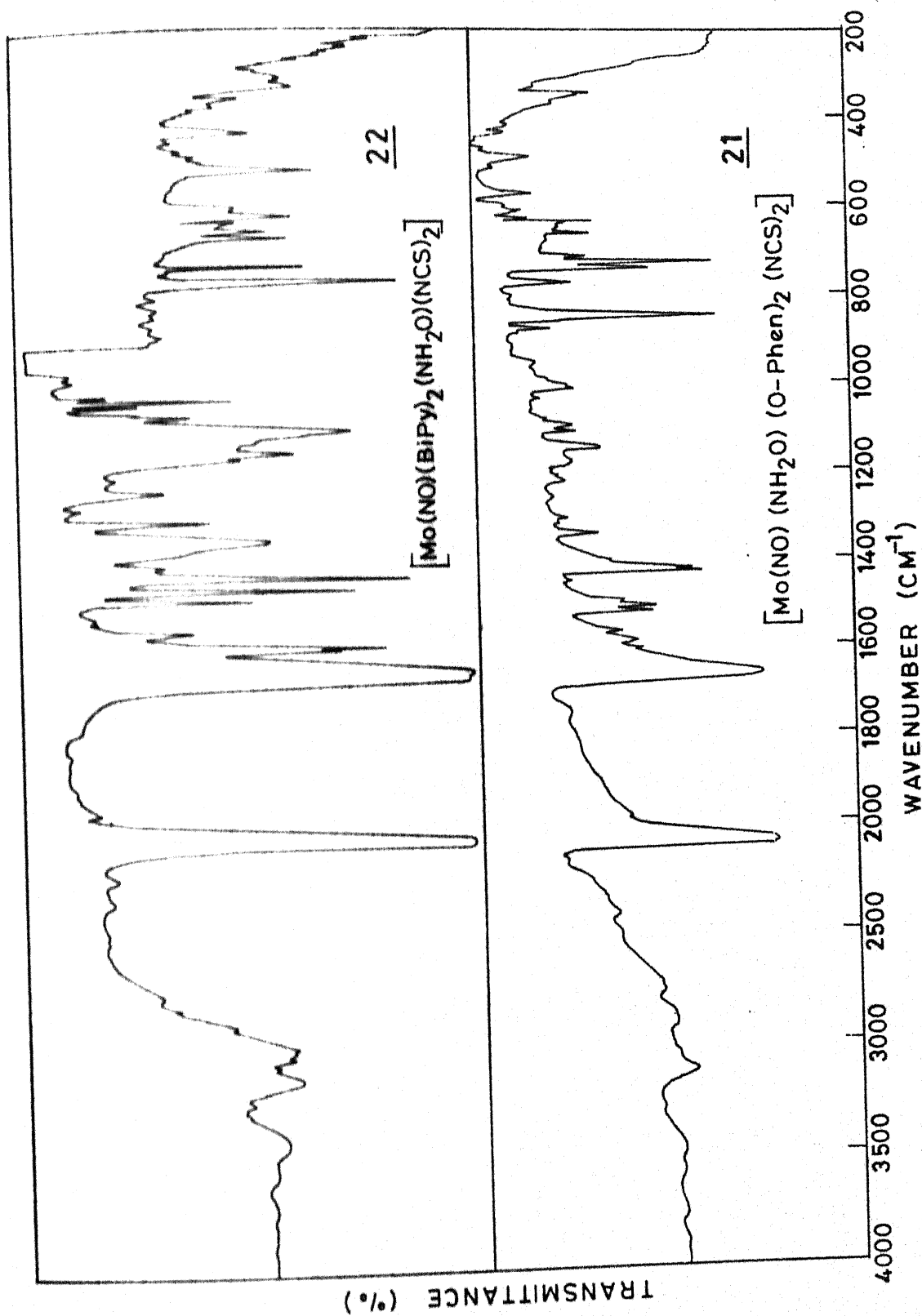
FIG. 3.10 · IR SPECTRA OF 17 & 19 .

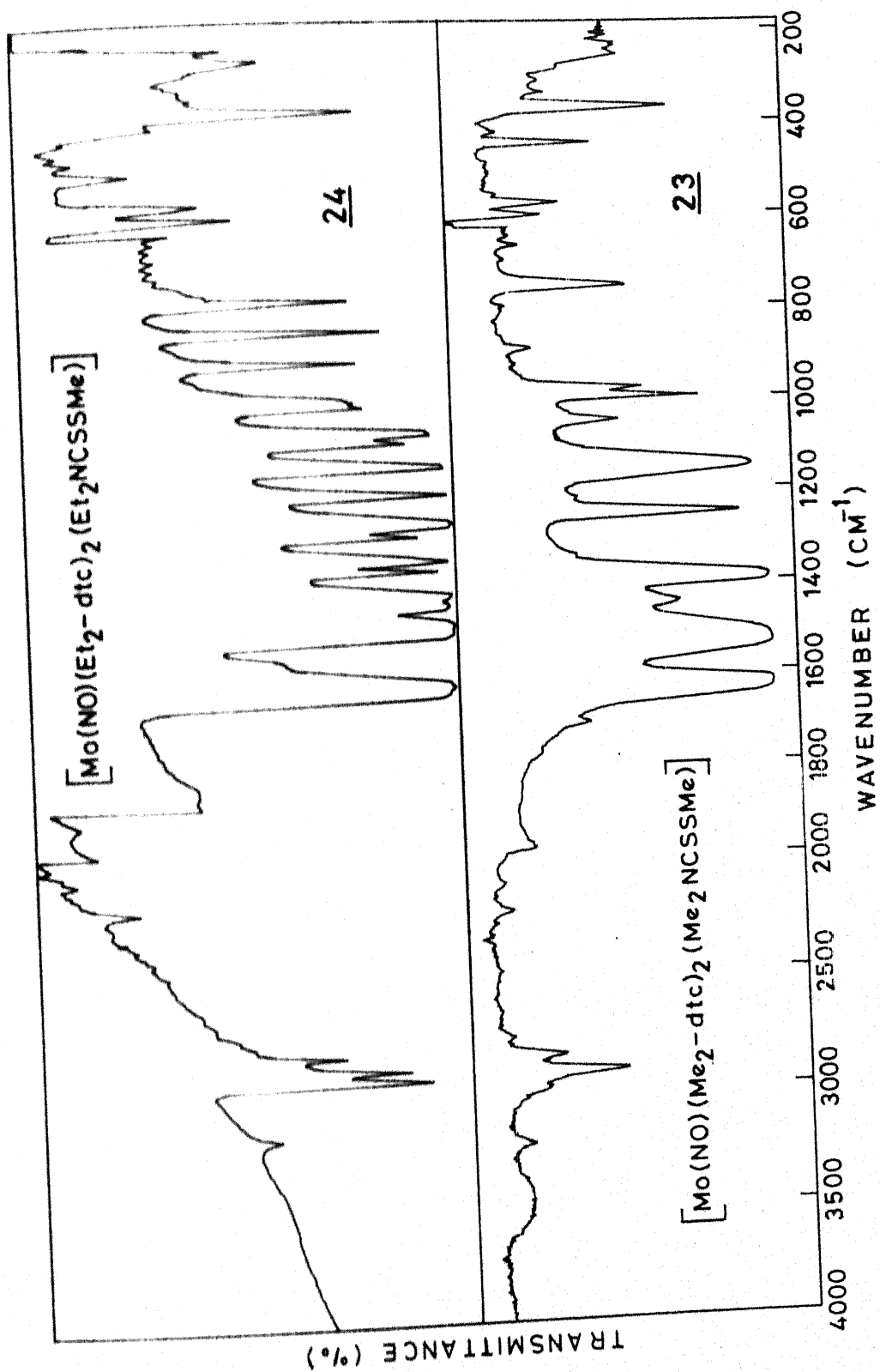FIG. 3.11 IR SPECTRA OF 21 & 22.

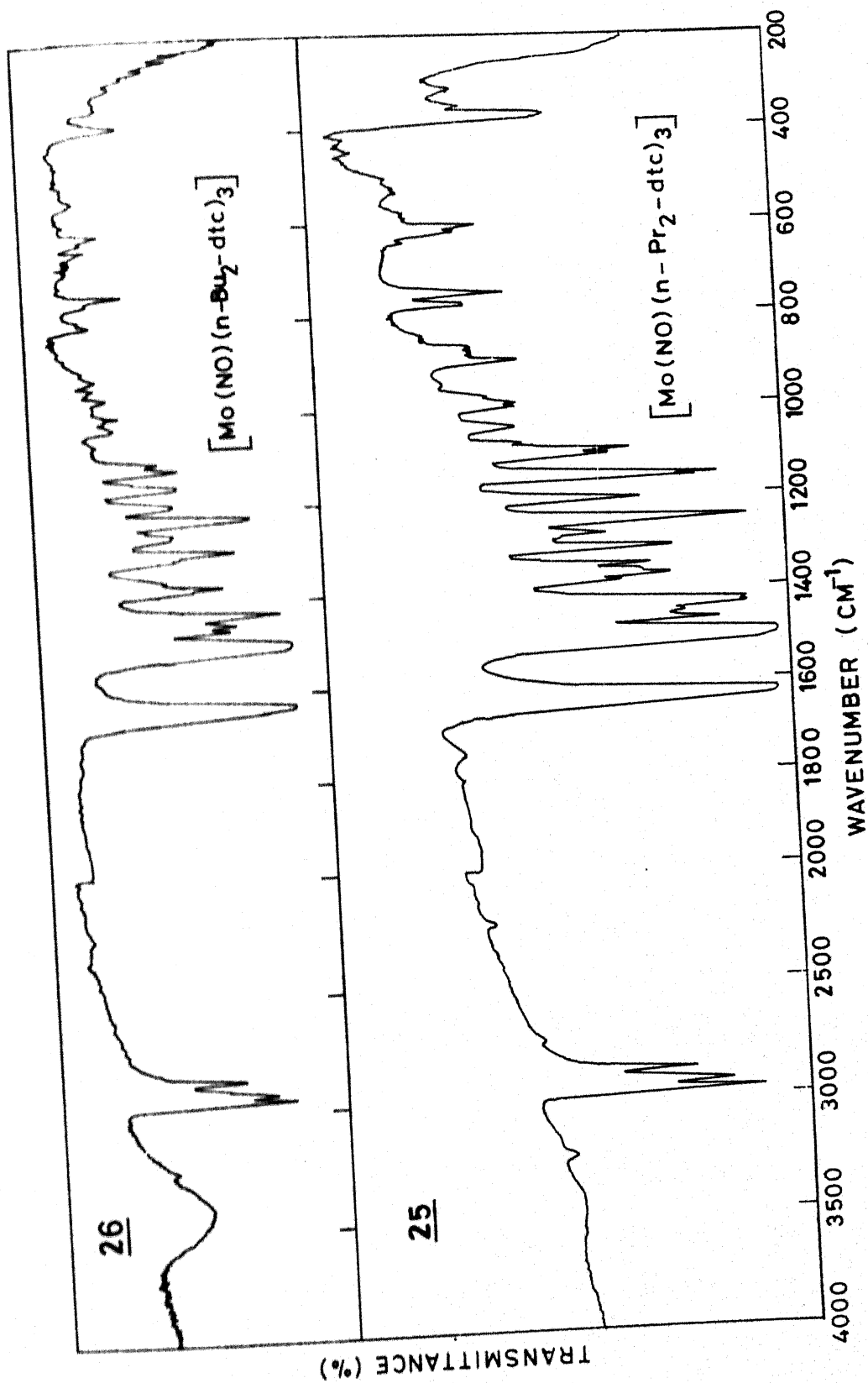FIG · 3.12 IR SPECTRA OF 23 & 24 .

93

FIG. 3.13 IR SPECTRA OF 25 & 26 .

presented in Table 3.2. Insensitivity of ν_{NO} to the overall charge of the complex as has been pointed out earlier has been observed in this instance also. Thus, for $[Cs_2 Mo(NO)Cl_4 \cdot H_2O]$ ν_{NO} appears at 1624 cm^{-1} [48] whereas for the cationic complexes like $[Mo(NO)(o\text{-phen})_2Cl]Cl$, the ν_{NO} appears at 1545 cm^{-1}. It may be a mere coincidence that a trend is observed in the location of the ν_{NO} in the successive redox series:

$\{Mo(NO)\}^6$, $\{Mo(NO)\}^5$ and $\{Mo(NO)\}^4$ at 1455 $(K_4[Mo(NO)(CN)_5])$ 1545 $([Mo(NO)(o\text{-phen})_2Cl]Cl)$ and 1676 cm^{-1} $(Cs_2[Mo(NO)Cl_5])$. However, any conclusion regarding the electronic distribution in the Mo-N-O group using the appearance of ν_{NO} at a particular wave number would be ill-founded.

Other Ligand Vibrations

For the dithiocarbamato complexes, it is well known that the bidentate or monodentate coordination of this type of ligand can be distinguished by monitoring the appearance of $\nu_{(C=N)}$ in the 1600-1450 cm^{-1} region and by the splitting of $\nu_{(CS)}$ near 1000 cm^{-1} [137]. When dithiocarbamate acts as a bidentate ligand the $\nu_{(C=N)}$ appears at higher (above 1485 cm^{-1}) region and when it is monodentate this stretch appears in the lower range. When there are several dtc ligands attached to the metal ion $\nu_{(C=N)}$ is not very much diagnostic of any unidentate coordination in the presence of bidentate mode of bonding.

Table 3.2

Sl. No.	Compound	ν NO (cm^{-1})	ν(Mo-N)/δ(Mo-N-C) (cm^{-1})	Other important vibrations (cm^{-1})
1.	Cs$_2$[Mo(NO)Cl$_4$·H$_2$O]	1624 (vs)	550 (w), 625 (m)	305 (s) ν(Mo-Cl)
2.	[Mo(NO)(o-phen)$_2$Cl]Cl	1545 (vs)	-	-
3.	[Mo(NO)(bipy)$_2$Cl]Cl	1555 (vs)	-	-
4.	Cs$_2$[Mo(NO)Cl$_5$]	1680 (vs)	580 (m), 610 (m)	325 (vs) ν(Mo-Cl)
5.	[Mo(NO)(Me$_2$-dtc)$_2$(Me$_2$NCSSMe)]	1640 (vs)	595 (m), 625 (m)	378 (s) ν(Mo-S)
6.	[Mo(NO)(Et$_2$-dtc)$_2$(Et$_2$NCSSMe)]	1650 (vs)	588 (m), 620 (m)	390 (s) ν(Mo-S)
7.	[Mo(NO)(n-Pr$_2$-dtc)$_3$]	1640 (vs)	590 (m), 625 (m)	385 (s) ν(Mo-S)
8.	[Mo(NO)(n-Bu$_2$-dtc)$_3$]	1640 (vs)	590 (m), 620 (m)	390 (s) ν(Mo-S)
9.	[Et$_4$N]$_2$[Mo(NO)(NH$_2$O)(NCS)$_4$]	1660 (vs)	-	-
10.	[Mo(NO)(NH$_2$O)(o-phen)$_2$(NCS)$_2$]	1680 (vs)	-	-
11.	[Mo(NO)(bipy)$_2$(NH$_2$O)(NCS)$_2$]	1675 (vs)	-	-

m, medium; s, sharp; vs, very sharp; w, weak.

A representative sample of this type of complex is
$[Ru(NO)(R_2-dtc)_3]$ in which one of the three dtc ligands is
coordinated in an unidentate manner. The appearance of a
shoulder band at 1490 cm^{-1} for this complex has been considered
suggestive of the unidentate coordination of the dithiocarba-
mate ligand. Sometimes, it is possible to identify the uni-
dentate coordination by the appearance of a doublet band around
1000 cm^{-1} responsible for $\nu_{(C-S)}$. However, methyl group has
absorption in this region and may overlap with these vibration
modes. The spectrum could get more complicated if bidentate
dtc group is already present in the complex.

Keeping the above in mind, the appearance of $\nu_{(C=N)}$ at
a higher wave number compared with that of the free ligand
suggests that the dithiocarbamato ligand is attached to molyb-
denum in a bidentate fashion. However, in the N,N-dimethyl-
dithiocarbamato complex for which we propose that one of the
three dtc is methylated to give an ester, $Me_2NCSSMe$, during
the course of preparation while acting as a bidentate ligand
(vide NMR spectra discussion). It is very difficult to identify
the presence of another methyl group in this ligand from the IR
spectrum. Furthermore, for this ester when it is bidentate,
one of the sulphurs would be tricoordinated instead of two.
Unfortunately, it would be very difficult to identify vibrations
due to this tricoordinated sulphur in the presence of other
modes of vibrations in the low frequency region.

Aromatic Diimines Vibrations

Coordination by o-phenanthroline and 2,2'-dipyridyl show characteristic spectral shifts in the region 900-500 cm^{-1} compared to the free bases. However, in the octa-coordinated complexes an alternative formulation with the assumption that one of the coordinated basic ligands may be protonated to give formulation like $[o\text{-phen-H}][Mo(NO)(NHO)(o\text{-phen})(NCS)_2]$. As the chelated hydroxylamido(-1) group contains acidic protons attached to nitrogen, removal of a proton is possible, to give the hydroxylamido(-2) group [103]. Under such conditions one could observe the absorption $[o\text{-phen-H}]^+$ from IR data. Mitchel has reported the appearance of a band at 2340 cm^{-1} for ($N\text{-}H^+$) stretching due to the presence of a bipyridylinium ion [139] and the observed spectra for both the compounds do not show the presence of any band in this region. Buckingham and co-workers [152] have reported IR data for a series of molybdenum complexes containing these ligands. They could distinguish the vibrations responsible for uncoordinated diiminium ions from the coordinated ones. A comparison between these data and the IR absorptions recorded for the present cases clearly suggests that no such protonated species exists in these compounds. The nonelectrolytic nature of these complexes further supports this observation.

Two interesting derivatives having the general composition $[Mo_2Cl_8(L\text{-}L)_2]$ (L-L = o-phen, bipy) have been synthesized starting from the intermediate compound $[NH_4]_3[Mo_2Cl_{11}]$

obtained from the denitrosylation reactions. The IR spectra of these complexes along with the parent complex are reproduced in Figs. 3.14 - 3.16.

The spectral data clearly indicate the presence of coordinated o-phen or bipy ligands in these complexes.

Metal-Chlorine Vibrations in Denitrosylated Complexes

$[NH_4]_3[Mo_2Cl_{11}]$ shows a very simple IR spectrum. Besides the absorption peaks responsible for ammonium ions, this spectrum shows a very strong band at 318 cm^{-1} which may be responsible for Mo-Cl stretch. The far infrared spectrum of this compound shows an additional band at 180 cm^{-1}. The appearance of a strong band at 180 cm^{-1} may be due to the presence of chlorine bridges or due to the presence of metal-metal bond. As all these compounds are diamagnetic in nature and the formal oxidation state of Mo is +4, the dimeric unit should contain Mo-Mo bond or chloro-bridge structure or both. However, nothing more can be said about these complexes till X-ray structural data are available.

Coordinated Hydroxylamido Vibrations

Wieghardt and coworkers reported the vibrational spectra of a series of oxamido complexes where the coordination of this anion takes place as side- on bonding [140]. Characteristic bands observed for this group in the range 3310-3200 cm^{-1} ($\nu_{(NH_2)}$), 1170 cm^{-1} ($\rho_{(NH_2)}$) and around 960 cm^{-1} ($\nu_{(N-O)}$).
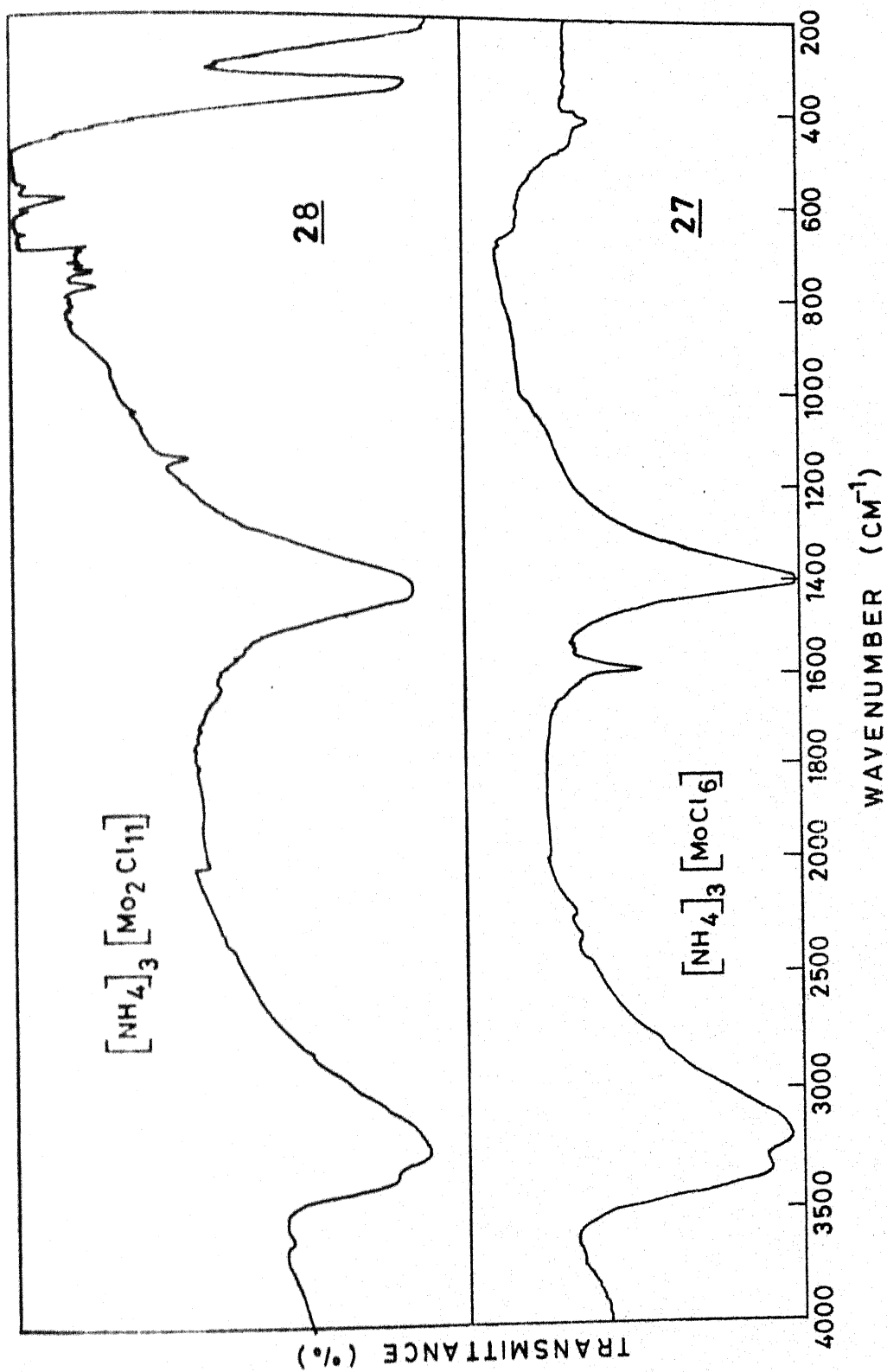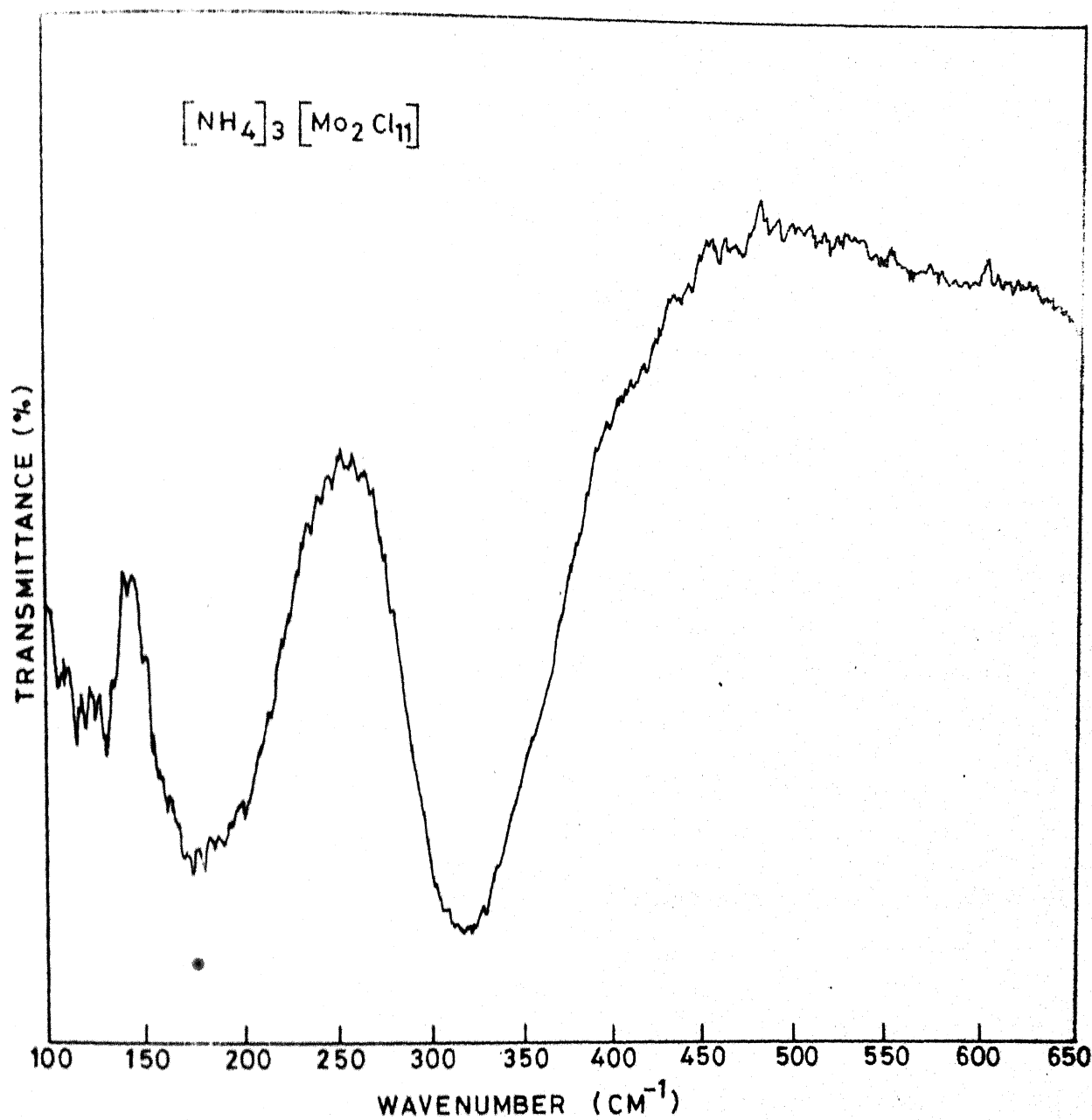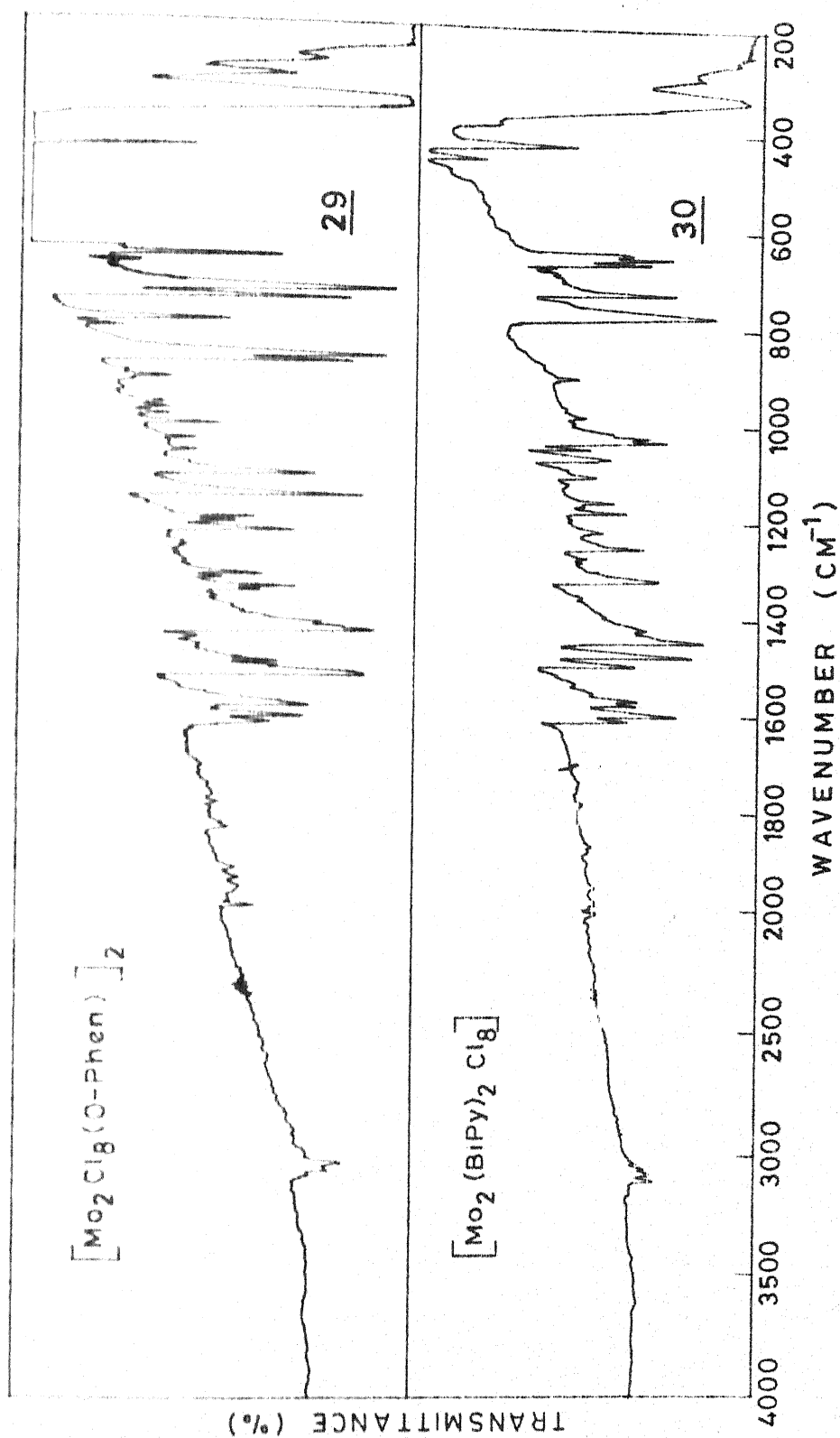
FIG. 3.14 IR SPECTRA OF 27 & 28.

99

FIG. 3.15   Far-IR SPECTRUM OF 24·

$[Mo_2 Cl_8 (O-Phen)]_2$

29

$[Mo_2 (BiPy)_2 Cl_8]$

30

TRANSMITTANCE (%)

WAVENUMBER (CM^{-1})

FIG. 3.16   IR   SPECTRA   OF   29   &   30.

In the spectrum of $[Et_4N]_2[Mo(NO)(NH_2O)(NCS)_4]$ (Fig. 3.10), the appearance of bands at 3200 cm^{-1}, 3080 cm^{-1}, 1130 cm^{-1} and a shoulder at 960 cm^{-1} may be attributed to $\nu(NH_2)$, $\rho(NH_2)$ and $\nu_{(N-O)}$ respectively.

^{1}H NMR Spectra of the Complexes

The ^{1}H-NMR spectra of some of the representative complexes are reproduced in Figs. 3.17 – 3.26. Assignments of ^{1}H-NMR absorptions relative to TMS are tabulated in Table 3.3. The spectral data for $[Mo(NO)_2(acac)_2]$, $[Mo(NO)_2(Me_2-dtc)_2]$ $[Mo(NO)_2(Et_2-dtc)_2]$ and $[Mo(NO)(n-Pr_2-dtc)_3]$ are identical to those reported earlier [141, 114] . For the derivatives $Mo(NO)_2Cl_2(\gamma-pic)_2$ and $Mo(NO)_2Cl_2(\beta-pic)_2$, IR spectra suggested the possibility of the following stereoisomers:
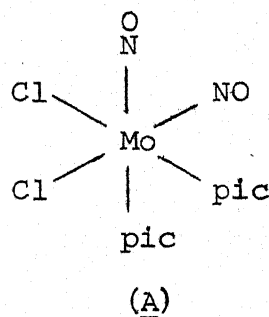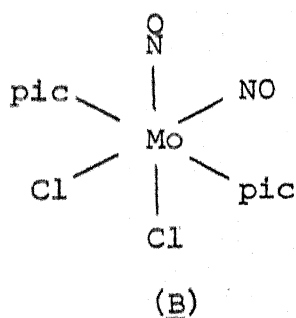
For the γ-picoline derivative the appearance of a singlet at 7.31 τ is clearly suggestive of the presence of the stereoisomer (B), whereas for the β-picoline derivative, a singlet at 7.5 τ and a doublet at 7.89 τ may be assigned for the presence of both the stereoisomers. The doublet arises
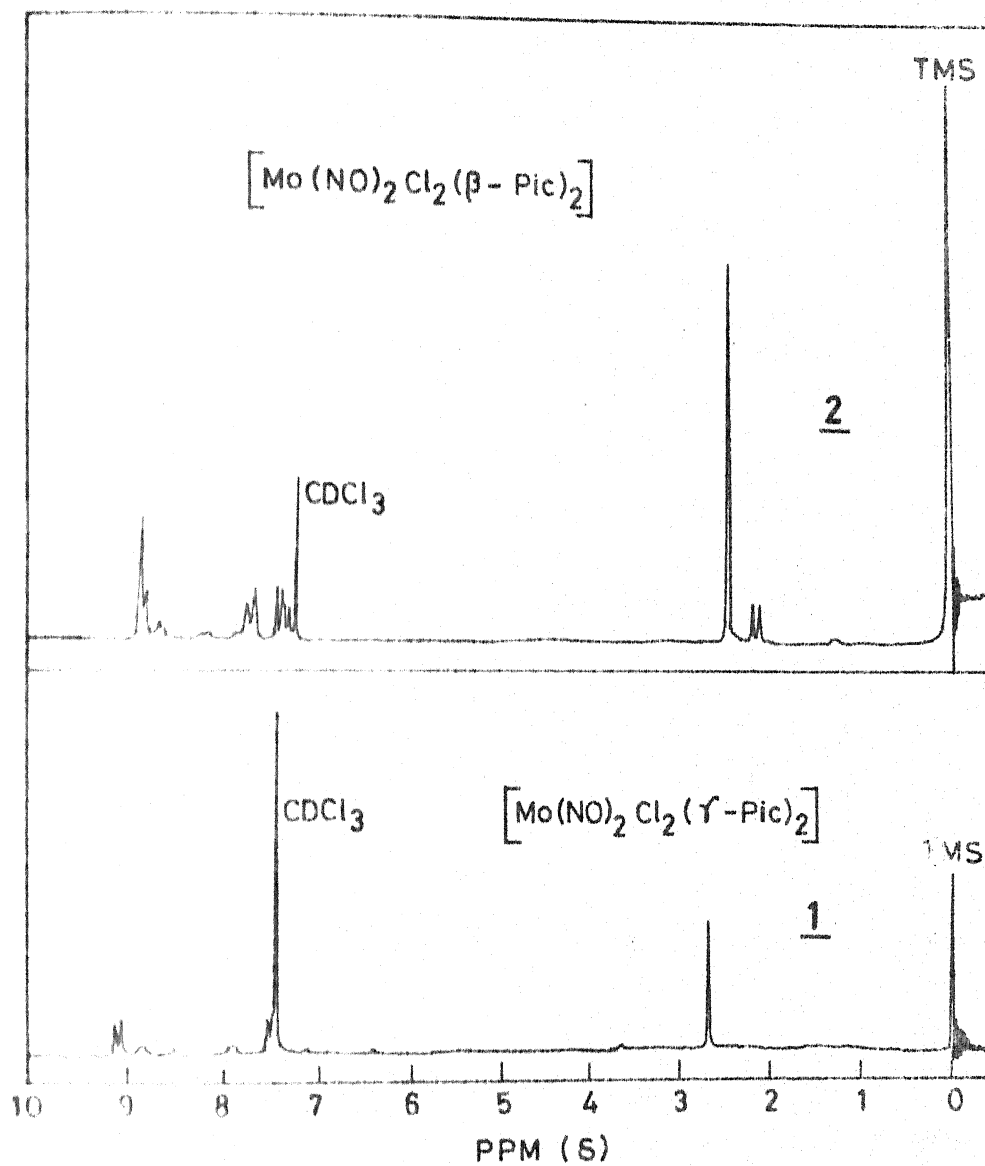
FIG. 3.17   NMR SPECTRA (100MHz) OF 1 & 2.

$[Mo(NO)_2(Me_2-dtc)_2]$
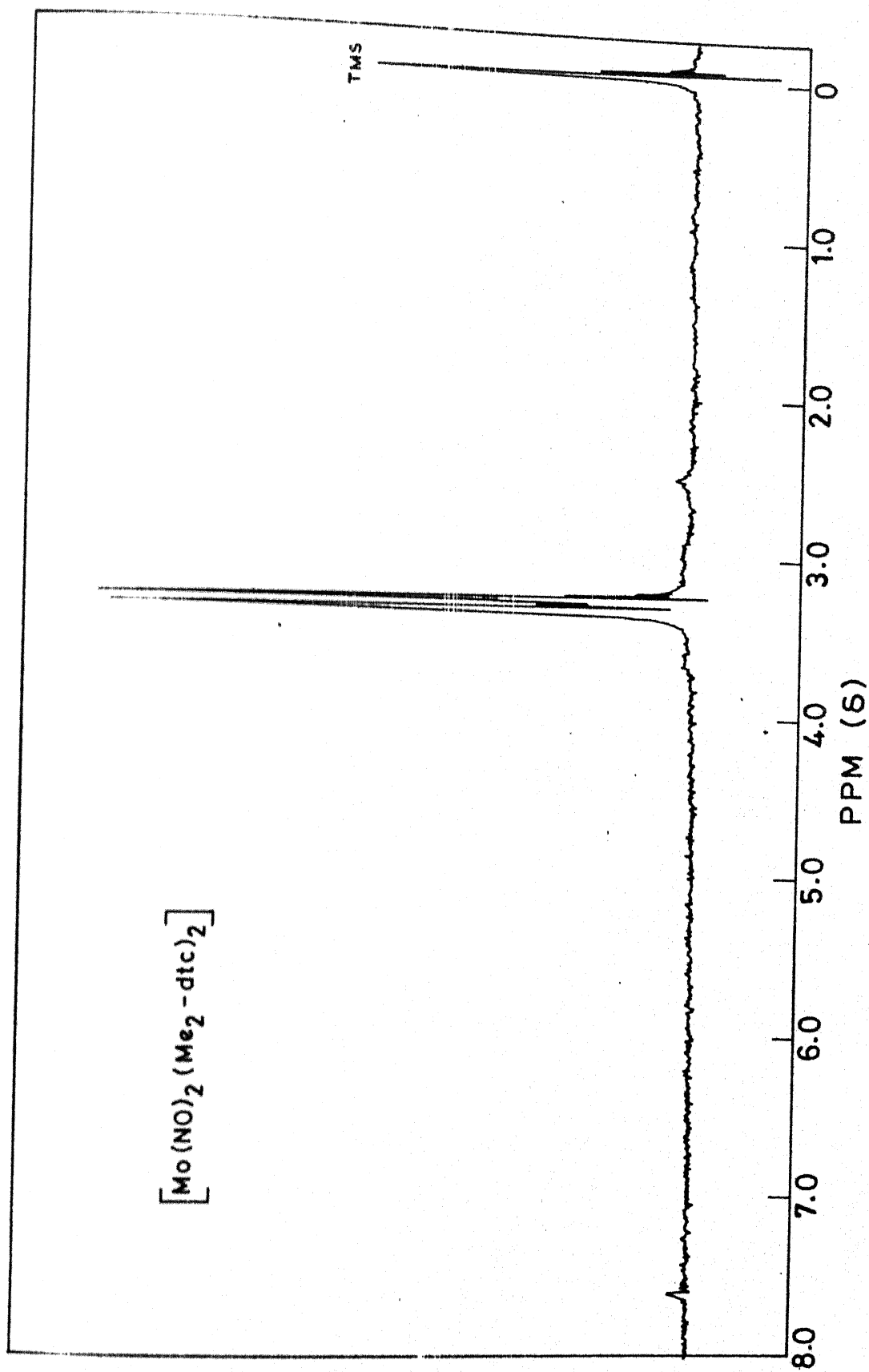
FIG·3.18 ^1H NMR SPECTRUM (60 MHz) OF 4.

$[Mo(NO)_2(Et_2-dtc)_2]$
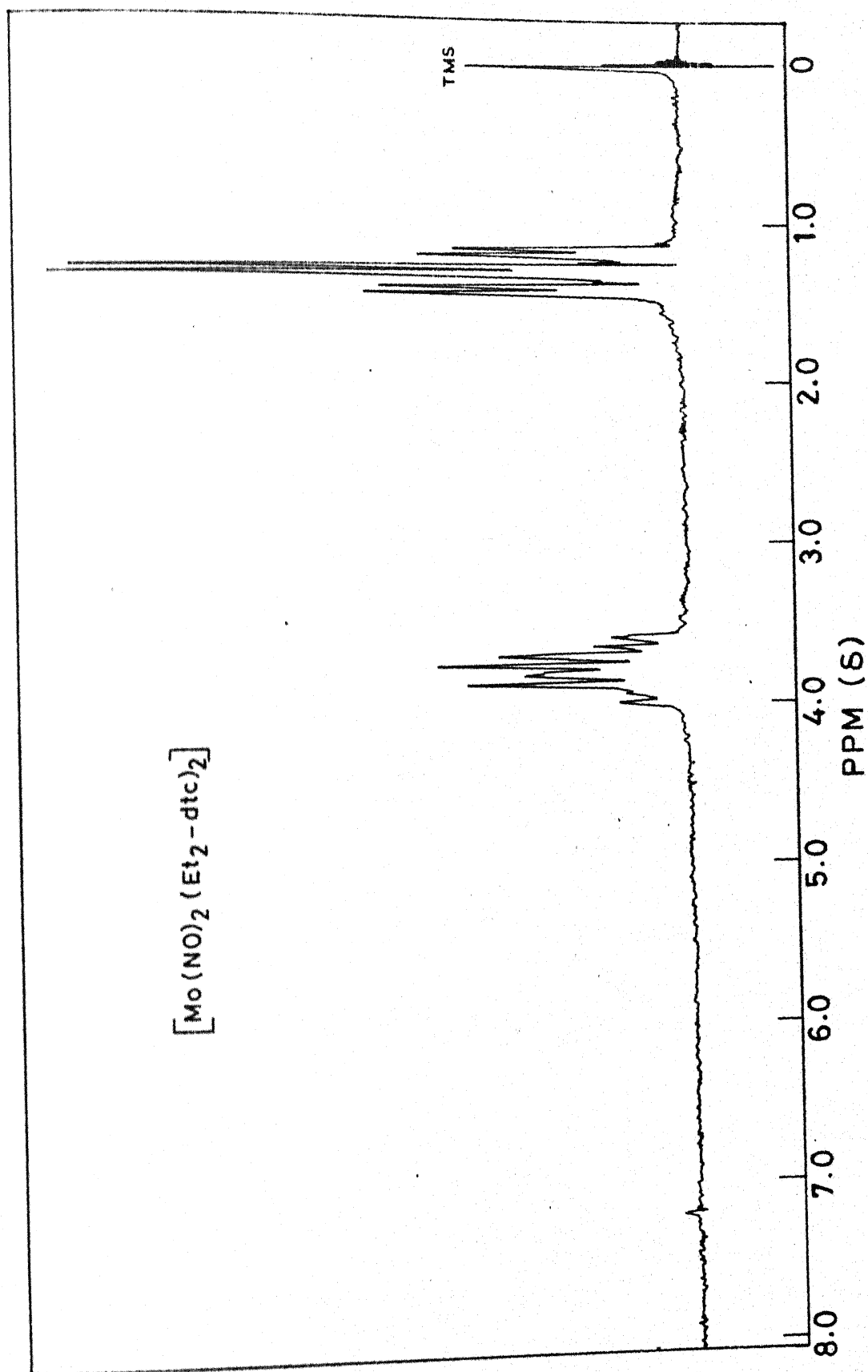
FIG.3.19 ^1H NMR SPECTRUM (60 MHz) OF **5** .

$[Mo(NO)_2(acac)_2]$
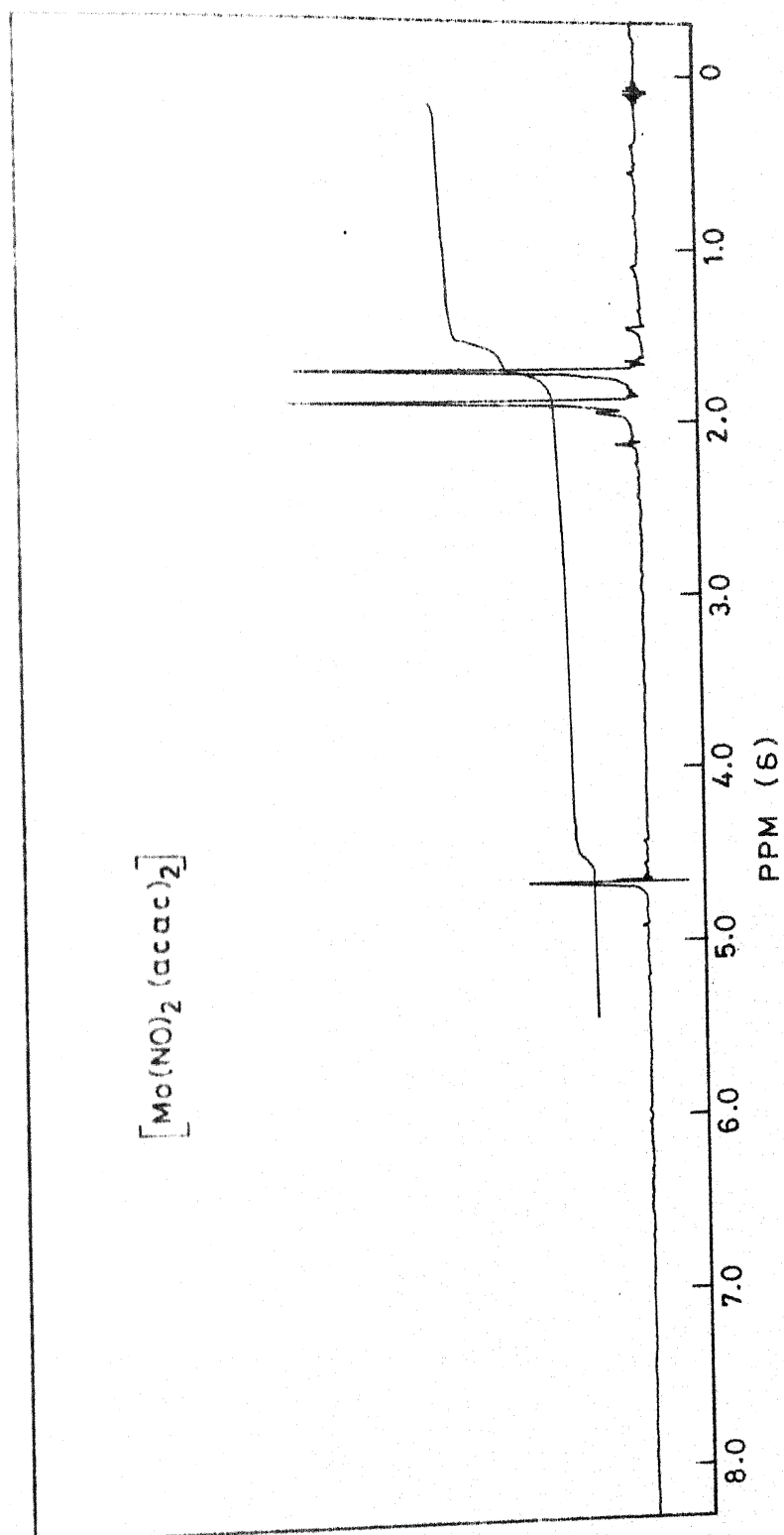
FIG. 3.20   NMR SPECTRUM (100 MHz) OF 7.

107
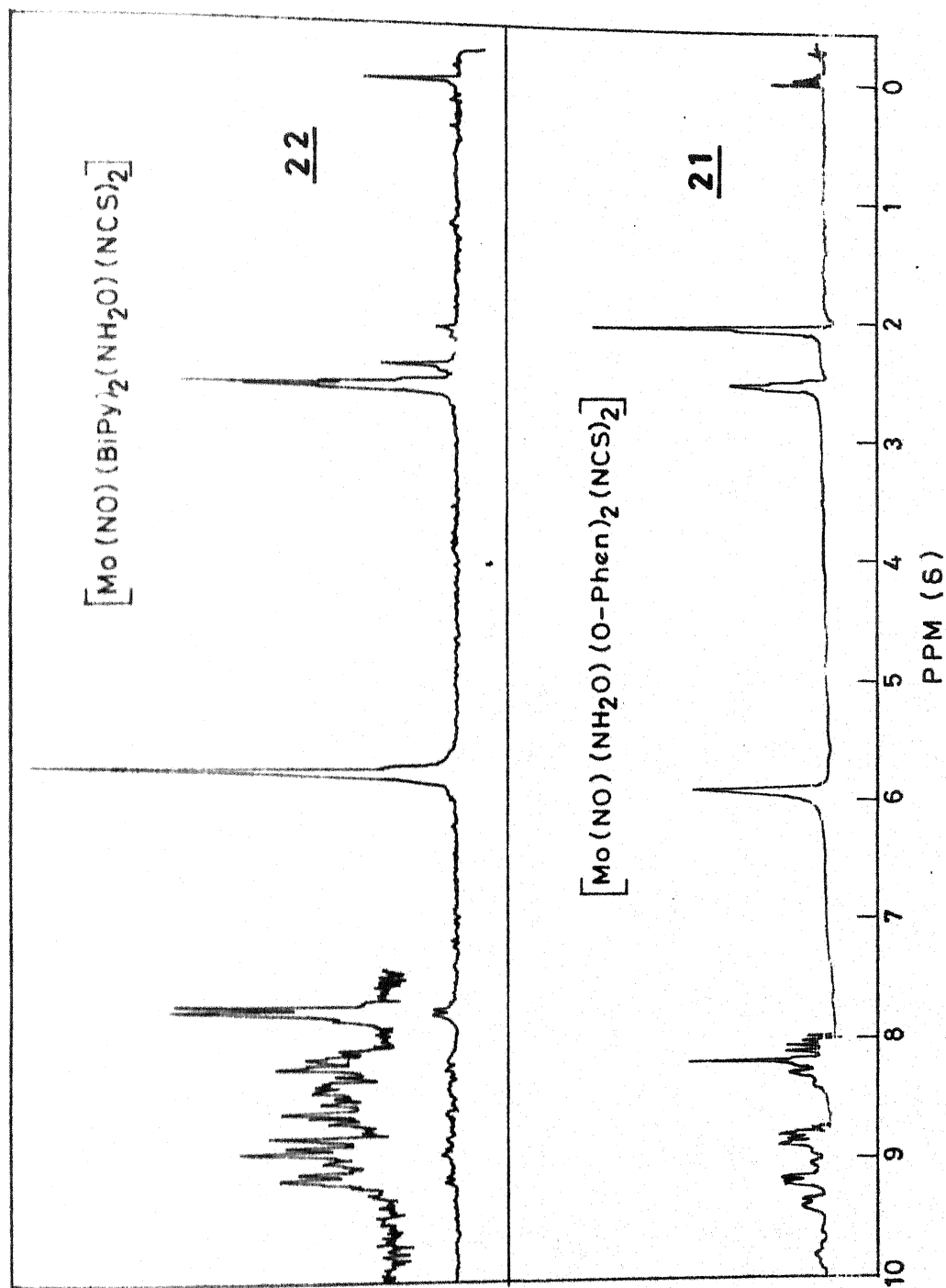
FIG. 3.21 ¹H NMR SPECTRA (100MHz) OF 21 & 22.
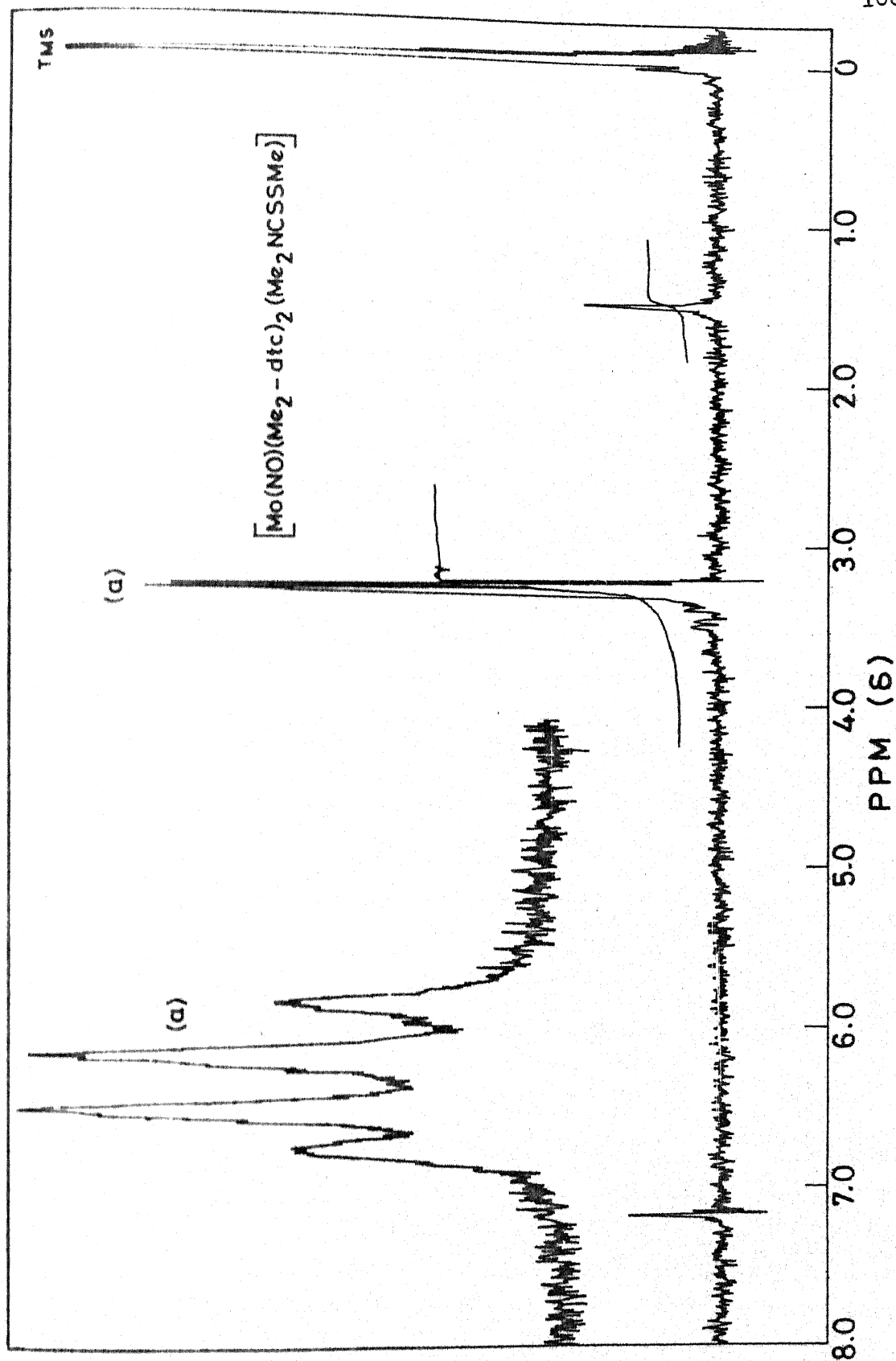
FIG. 3.22 ^{1}H NMR SPECTRUM (60 MHz) OF 23.

$[Mo(NO)(Me_2-dtc)_2(Me_2NCSSMe)]$

$[Mo(NO)(Et_2\text{-}dtc)_2(Et_2NCSSMe)]$
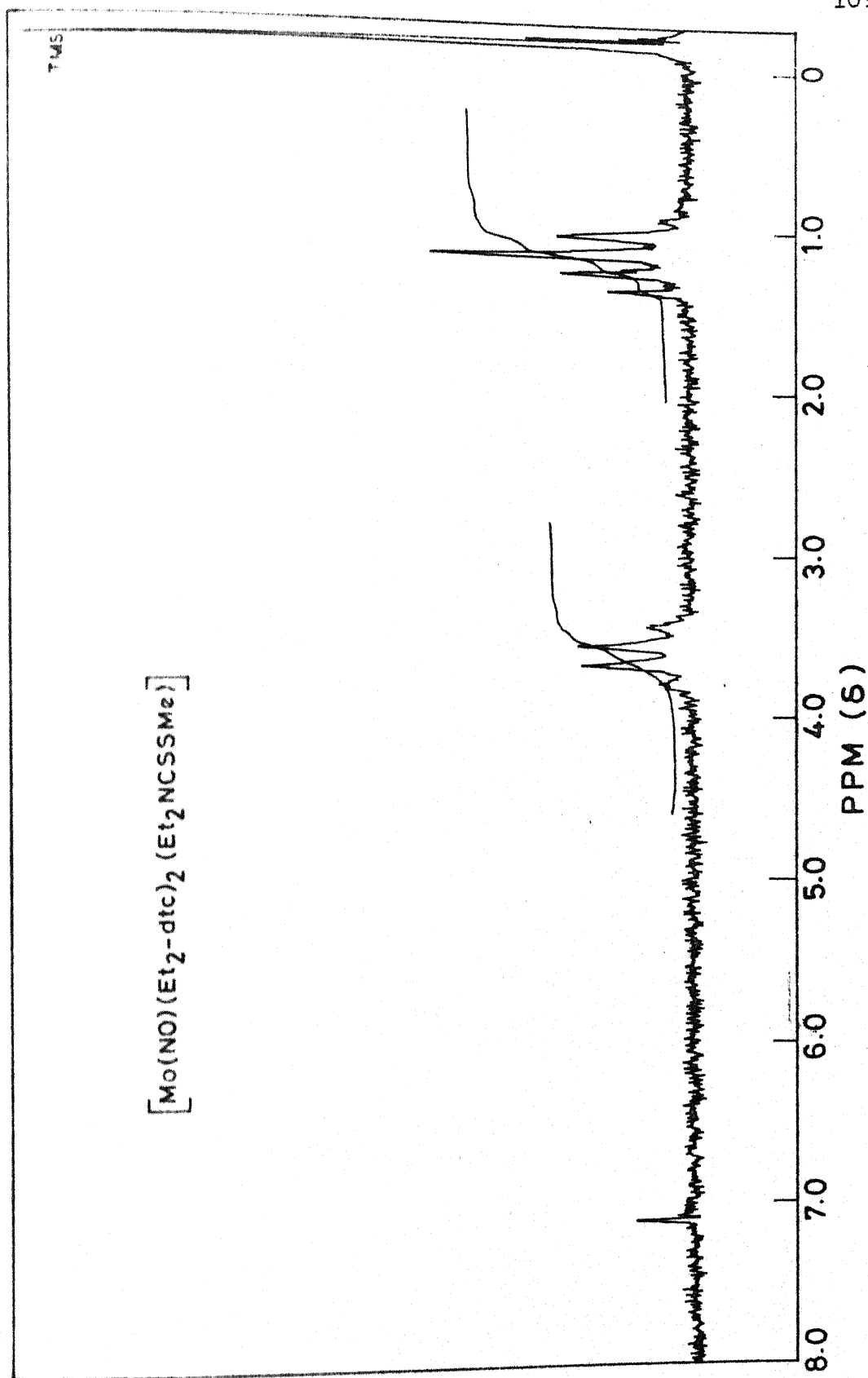
FIG. 3.23 ^1H NMR SPECTRUM (60 MHz) OF <u>24</u> .

PPM (δ)

$[Mo(NO)(n-Pr_2-dtc)_3]$
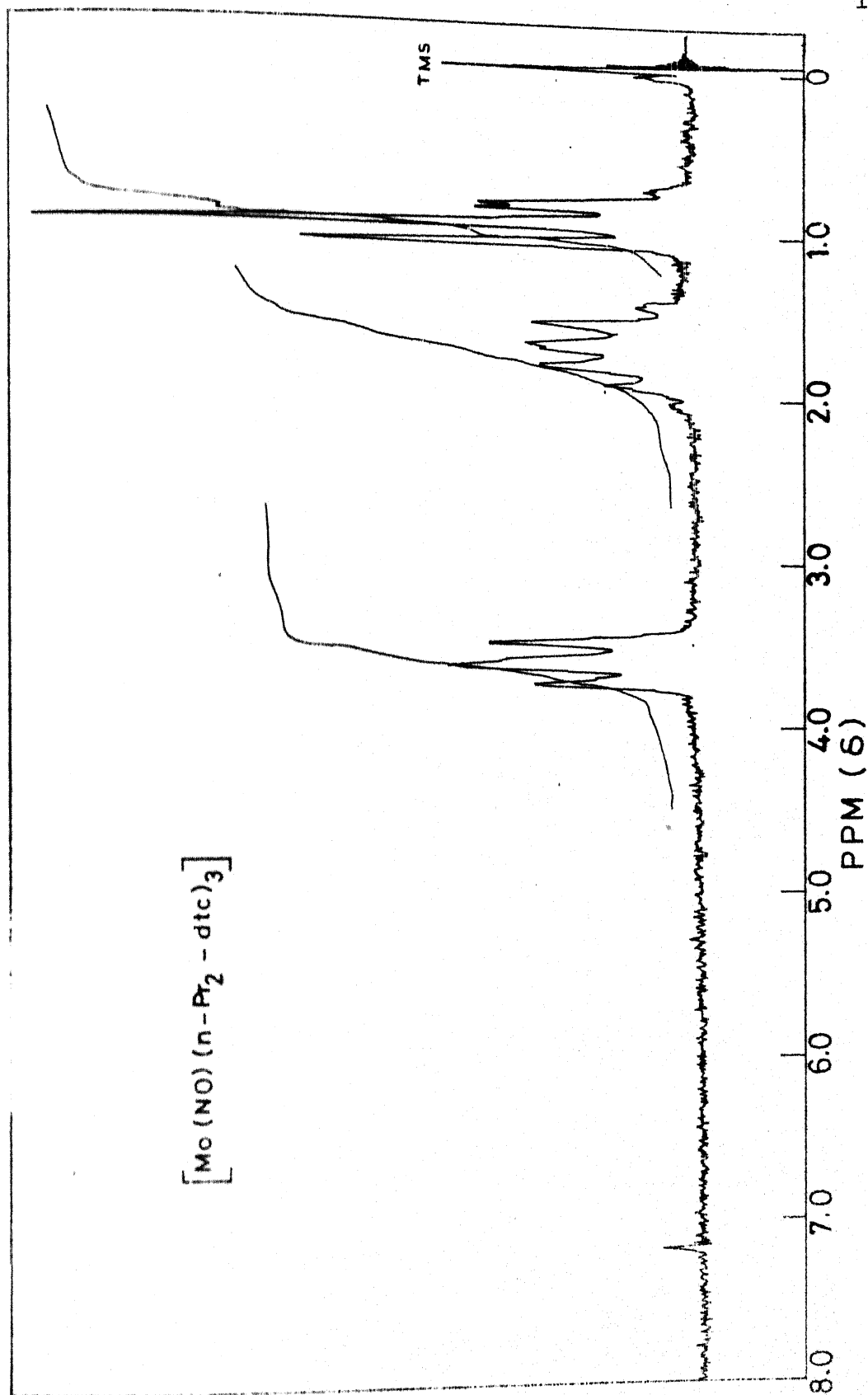
FIG. 3.24   NMR SPECTRUM (60 MHz) OF 25 .

Table 3.3

Sl. No.	Compound	^{1}H-NMR absorption (τ)	Relative intensity	^{13}C-NMR absorp (ppm)
1.	$[Mo(NO)_2Cl_2(\gamma\text{-pic})_2]$	7.31(s)	–	–
2.	$[Mo(NO)_2Cl_2(\beta\text{-pic})_2]$	7.57(s), 7.89(d)	–	–
3.	$[Mo(NO)_2(acac)_2]$	4.40(s), 7.80(s), 8.02(s)	2:6:6 (CH:CH$_3$:CH$_3$)	27.62, 26.81 102.0 (C–H); 191.0, 190.5
4.	$[Mo(NO)_2(Me_2\text{-dtc})_2]$	6.67(d)	1:1 (N–Me)	
5.	$[Mo(NO)_2(Et_2\text{-dtc})_2]$	6.12(8), 8.72(6)	2:3 (N–CH$_2$:–CH$_3$)	
6.	$[Mo(NO)_2(Me_2\text{-dtc})_2(Me_2NCSSMe)]$	6.7(q), 8.48(s)	6:1 (N–Me:S–Me)	203.12 : 202.22 quaternary car' (1:2) 40.7, 40.39, 38 37.51 (1:1:2:2) N–Me 32.6 (S–Me)
	$[Mo(NO)(Et_2\text{-dtc})_2(Et_2NCSSMe)]$	6:25 (q), 8.49(s), 8.73 (τ)	12:3:18 (N–CH$_2$:S–Me:–CH$_3$)	–
	$[Mo(NO)_2(n\text{-}Pr_2\text{-dtc})_3]$	4.44(m), 8.34(m), 9.03(m)	Complex	–
9.	$[Mo(NO)_2(NH_2O)(o\text{-phen})_2(NCS)_2]$	4.10(s), 7.95(s)	–	–
10.	$[Mo(NO)_2(bipy)_2(NH_2O)(NCS)_2]$	4.22(s), 7.68(s)		

s, singlet; d, doublet; t, triplet; q, quartet; m, multiplet; 6, sextuplet and 8, octet. $\tau = (10 - \delta)$; δ= ppm.

due to the presence of two β-picolines. The presence of 80%
of (B) and 20% of (A) stereoisomers was calculated by integra-
tion. Thus, it is apparent that this method is not stereo-
specific. An explanation for this may be given as follows.
The dinitrosylation stage occurs only after the formation of
mononitrosylmolybdenum moiety. The moninitrosyl moiety changes
to dinitrosylmolybdenum species by two separate reactions:
(i) disproportionation of $\{Mo(NO)\}^4$ to $\{Mo(NO)_2\}^6$ and (ii)
conversion of $\{Mo(NO)\}^4$ to $\{Mo(NO)(NH_2O)\}^4$ followed by step-
wise deprotonation to give $\{Mo(NO)_2\}^6$. However, the dispropor-
tionation reaction occurs preferentially in acidic medium whereas
the stepwise deprotonation of oxamido group (NH_2-O^-) takes place
at nearly neutral medium. For the isolation of these complexes,
final acidification step (vide supra) may involve some dispro-
portionation reaction and any proposal for the mechanism of the
formation of the different stereoisomers is not possible at
this stage.

    [Mo(NO)(Me$_2$-dtc)$_2$(Me$_2$NCSSMe)] and [Mo(NO)(Et$_2$-dtc)$_2$-
(Et$_2$NCSSMe)] show a quartet around 6.7τ, a singlet at 8.48 τ
and a quartet around 6.25τ, a singlet at 8.49τ and a triplet
around 8.73τ respectively. For the methyl derivative, the
ratio of the two signals is 6:1 which is attributed to the
presence of seven methyl groups in total. The appearance of
the quartet around 6.7τ is originating due to the methyl groups
attached to the nitrogen of the dithiocarbamate ligands. This

range is well established for complexes of N,N -dimethyldithio-carbamates and even in $[Mo(NO)(Me_2-dtc)_3]$[114]. This singlet methyl group at 8.48 comes at a higher field to that expected for CH_3SSR group [142]. As this sulphur is coordinated to molybdenum, its shielding character increases resulting in the appearance of this singlet to higher value for the thioester group.

Complex $[Mo(NO)(NH_2O)(bipy)_2(NCS)_2]$ is soluble in DMSO and hence its ^{1}H-NMR spectrum in D_6-DMSO was taken (Fig. 3.21). We have tried to decide the bonding mode of oximido ligand. If we assume that it is bidentate $Mo{<}{\overset{N\overset{\textstyle H}{}}{\underset{O}{|}}}{}^{H}$ group must exist which is equivalent to cyclic amines and in this case, the expected singlet should come in the high field region (7.0 to 9.5 τ). This spectrum shows a strong singlet at 4.10 τ for NH_2 and a weak singlet at 7.95 τ. We interpret the former singlet as originating from the unidentate hydroxylamido group. However, the weak singlet appearing at 7.95 τ may be responsible for the formation of a bidentate hydroxylamido group with the release of a dipyridyl from the coordination sphere. This partial rearrangement can be expressed as follows:

$$[Mo(NO)(NH_2O)(bipy)_2(NCS)_2] \xrightarrow{\text{DMSO}} [Mo(NO)(NH_2O)(bipy)(NCS)_2] + bipy$$

(unidentate)   (bidentate)
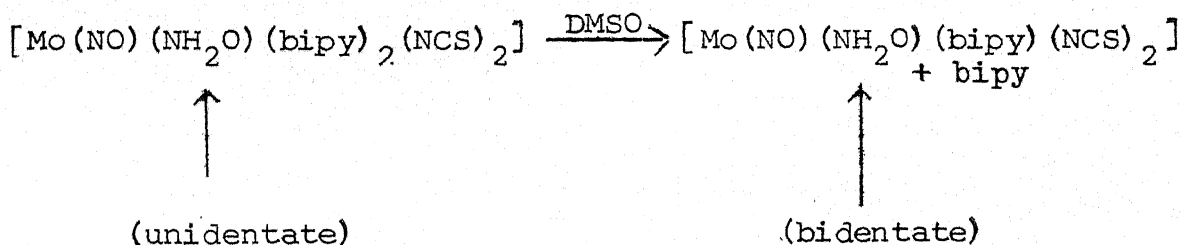
The bipy-derivative is not freely soluble in DMSO and to get a solution for recording the NMR spectrum, slight warming was necessary. We presume that while warming, the rearrangement outlined above took place. The corresponding o-phenanthroline derivative is still less soluble compared to the bipyridyl analog and to get a solution in DMSO, strong heating is necessary. As drastic condition is employed for its dissolution, its NMR spectrum shows a stronger singlet at 7.63τ which must be due to the bidentate hydroxylamido group. The relatively less intense singlet (4.22τ) has been assigned to the unchanged starting complex where hydroxylamido group is unidentate. The release of free aromatic diimine was confirmed by adding Fe^{2+} ion. These complexes in DMSO, on boiling generated red colour of $[Fe(o\text{-}phen)_3]^{2+}$ or $[Fe(bipy)_3]^{2+}$.

The rapid exchange of proton on the nitrogen atom has been observed with D_2O and accounts for the appearance of a sharp singlet.

^{13}C-NMR Spectra

The proton decoupled ^{13}C-NMR spectrum of $[Mo(NO)(Me_2\text{-}dtc)_2\text{-}(Me_2NCSSMe)]$ substantiate the assignments made from ^{1}H-NMR data. The spectrum is reproduced in Fig. 3.26 which shows 5 methyl resonances (two of which are twice the intensity) in the range 40.7 - 32.6 ppm related to TMS. The more intense peaks at 38.26 and 37.51 ppm must be resulting from four methyl groups
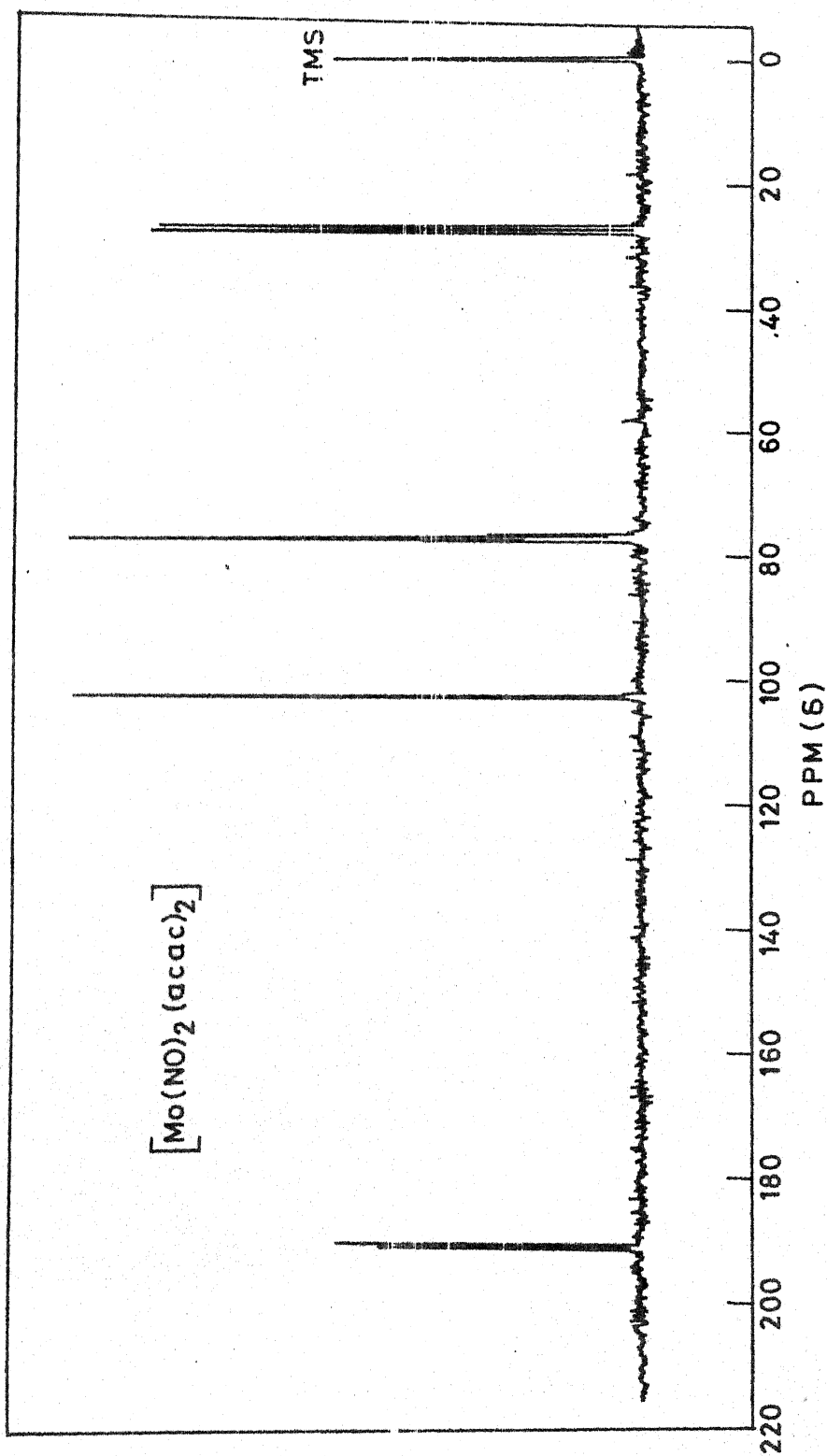
115

FIG.3.25 ^{13}C NMR SPECTRUM (67.89 MHz) OF _7_.
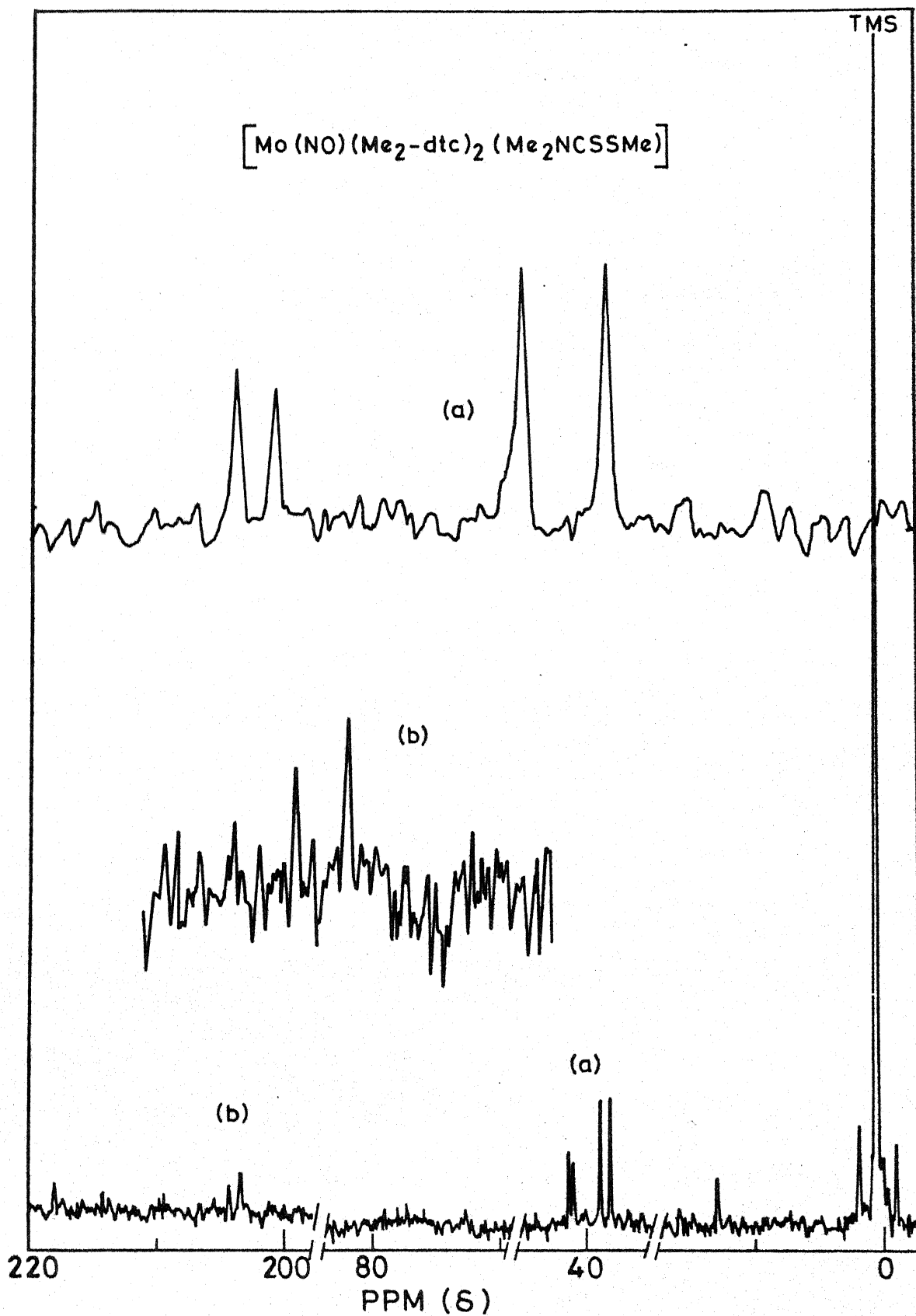
FIG.3.26 ^{13}C NMR SPECTRUM (67.89 MHz) OF 23 .

of two bidentate dithiocarbamato ligands attached to the molybdenum in the equitorial base. The peaks at 40.7 and 40.36 ppm must be resulting from the two methyl groups attached to the nitrogen of the bidentate methylester of N,N-dimethyldithiocarbamato ligand whose one end is attached to the molybdenum roughly trans- to the nitrosyl group and the other bite may be slightly above or below the equitorial base. The peak at 32.6 ppm may thus be assigned to the methyl group attached to the sulphur of the methyl ester. Two quarternary carbon resonances (one of twice the intensity, indicating accidental superposition) appear at 203.1 and 202.2 ppm. It is interesting to note that the resonances of the quaternary carbons are much weaker than those of the other carbon atoms and so to detect the signal, paramagnetic species are added to decrease T_1 relaxation time of quaternary carbon nuclei [138]. However, we have observed that these signals can be readily detected using a high frequency (67.89 MHz) spectrometer even without the addition of any paramagnetic species. The more intense peak at 202.2 ppm has been assigned to the quaternary carbons of the two bidentate N,N-dimethyldithiocarbamato ligands. These results followed by steric requirements suggest the structure of the complexes to be as shown below.

The proton decoupled ^{13}C spectrum of $[Mo(NO)_2(acac)_2]$ has been reproduced in Fig. 3.25. This shows two CH_3, one CH and two CO carbon peaks at 26.8, 27.6; 102.0 and 190.5, 196.0 ppm respectively.
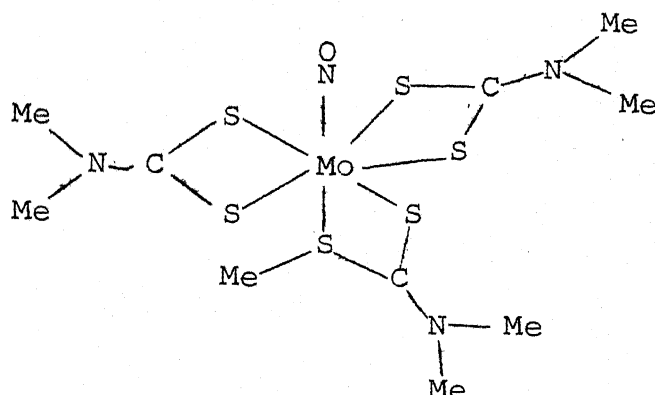
X-Ray Photoelectron Study

The electronic distribution in an M-N-O group lies in between the two extreme descriptions NO^+ and NO^-. X-ray photoelectron spectroscopy may thus help to study the binding energies of electrons of the atoms in chemical compounds. The change in binding energies for a particular atom present in a functional group when free and coordinated may reflect on the change of electron distribution of the atom on coordination. A positive shift corresponds to the effective positive charge of an atom in the compound and the negative shift corresponds to the effective negative charge. The 1s nitrogen binding energy for the coordinated nitrosyl group in $Cs_2[Mo(NO)_2Cl_4]$ has been recorded and this spectrum is reproduced in Fig. 3.27. For comparison, the N1s binding energy values for some representative nitrosyl complexes along with N1s value for NO^+ in $NO^+ClO_4^-$ and for neutral NO molecule are listed in Table 3.4. ESCA data (Table 3.4) show that with the possible exception of
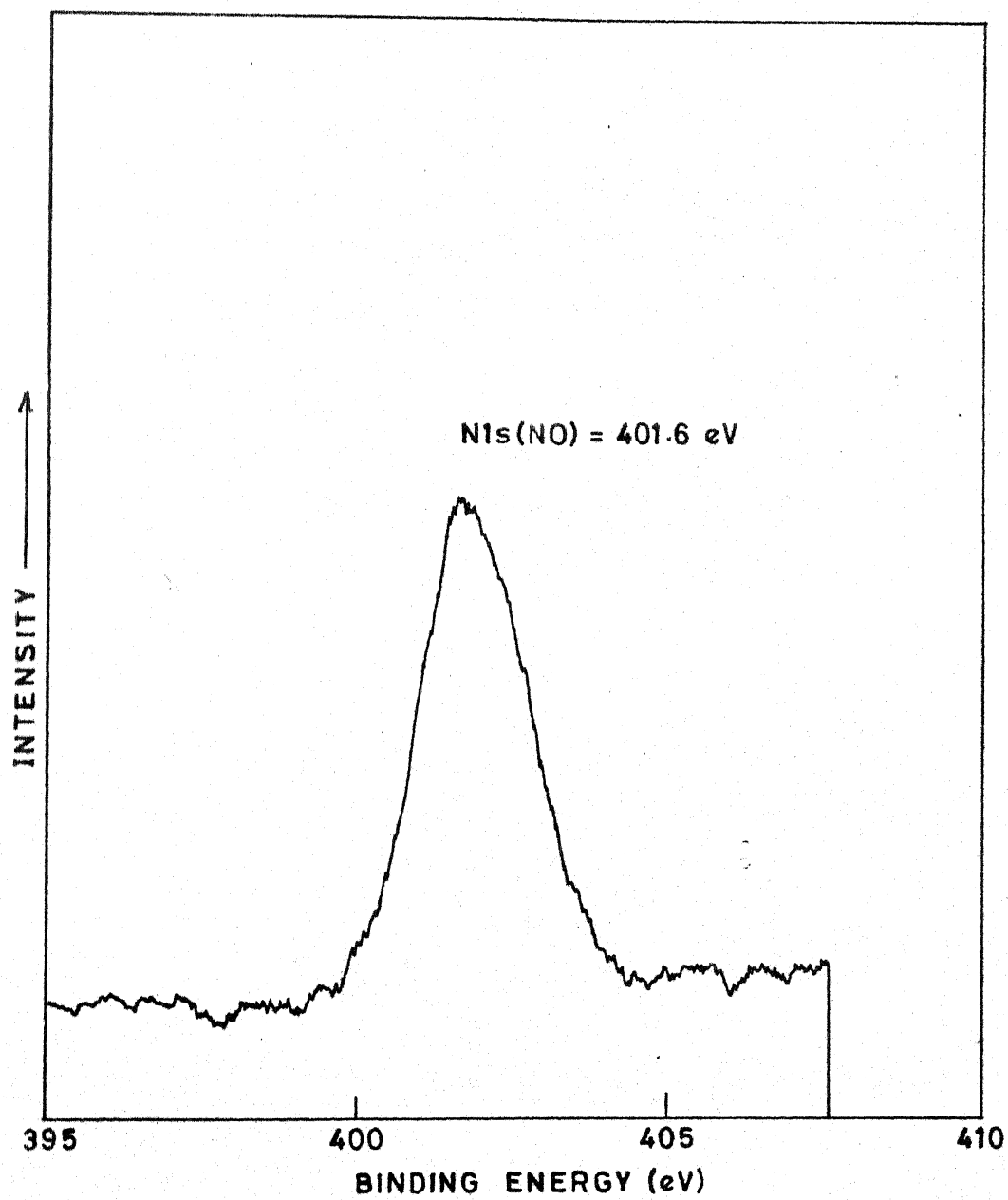
FIG. 3.27 X-RAY PHOTOELECTRON SPECTRUM OF
$Cs_2\left[Mo(NO)_2 Cl_4\right]$

Table 3.4

Sl.No.	Species	N1s(NO) eV	Reference
1.	$NO^+ ClO_4^-$	409.0	[149]
2.	NO (as gas)	406.0	[149]
3.	NO^{-*}	402.0	[149]
4.	$Na_2[Fe(NO)(CN)_5]$	403.6	[149]
5.	$Fe[Fe(NO)(CN)_5]$	402.6	[149]
6.	$[Mo(NO)_2Cl_2(PPh_3)_2]$	401.6	[144]
7.	$[Mo(NO)_2(Et_2-dtc)_2]$	400.0	[145]
8.	$[Mo(NO)_2Cl_2(diars)]$	401.6	[145]
		401.2	
9.	$Cs_2[Mo(NO)_2Cl_4]$	401.6	This work

*Extrapolated value.

$[Fe(NO)(CN)_5]^{2-}$, the N1s binding energies for all other nitrosyl complexes come lower to that of NO^- and even for the nitroprusside, the value is lower than that of neutral NO. This strongly suggests that all nitrosyl complexes reported in this thesis can be treated as containing NO^-. However, from the consideration of assigning the oxidation state of the metal atom in a nitrosyl complex, binding energies of a particular metal can be compared as a function of the different oxidation states. For a series of molybdenum complexes $3d_{5/2}$ binding energies are tabulated in Table 3.5.

From the above table, it is clear that Mo $3d_{5/2}$ binding energy gradually increases with increase in oxidation state of molybdenum where ligand environments are non-controversial. Also whenever the complex is in anionic form this binding energies is a bit higher than that of a neutral complex having the same oxidation state of molybdenum. Thus the overall charge on the complex has a noticeable effect on the binding energies. Thus based on the reported Mo $3d_{5/2}$ binding energies of some of the neutral ${Mo(NO)_2}^6$ derivatives, slightly higher values in the case of $Cs_2[Mo(NO)_2Cl_4]$ is justified. Brant and Feltham [145] comparing the binding energy for $[Mo(NO)_2Cl_2(diars)]$ with trans-$[MoOCl(diars)_2]PF_6$ (230.1 eV) concluded that as this dinitrosyl derivative is having slightly higher value for Mo $3d_{5/2}$, the formal oxidation state of molybdenum in this complex may be taken as +5. However, the binding energy of molybdenum in the

cationic complex should be viewed with caution as the overall positive charge may affect the observed value. For a series of neutral complexes containing $\{Mo(NO)_2\}^6$ moiety, the Mo $3d_{5/2}$ binding energies fall below those reported for the pentavalent molybdenum and as Walton [146] showed, the binding energy for Mo(V) may even be equal to that of Mo(IV). On these grounds the oxidation state of molybdenum in these series may be considered as +4. This is in conformity with the assignment of nitrosyl groups as NO^-. However, the situation is not so simple as it appears from the above discussion. For example in the iron series: $K_4[Fe(CN)_6]$, $K_3[Fe(CN)_6]$ and $Na_2[Fe(NO)(CN)_5]$; the Fe $2p_{3/2}$ binding energies reported are 708.8, 710.3 and 711.0 eV respectively [149]. Since the oxidation state of iron is +2 and +3 in ferrocyanide and ferricyanide respectively, the oxidation state of iron should be more than +3 in nitroprusside.

Magnetic Properties of the Complexes

As expected, complexes of the series containing $\{Mo(NO)_2\}^6$ and $\{Mo(NO)\}^4$ moieties are diamagnetic in nature. Compounds containing $\{Mo(NO)\}^5$ configuration are paramagnetic with respect to one unpaired electron. The magnetic moment values of the newly prepared complexes along with a few other reported compounds are presented in Table 3.6.

<u>Table 3.6</u>

Sl. No.	Compound	μ_{eff} (BM)	Reference
1.	$[(C_6H_6)_2Mo]I$	1.74	[153]
2.	$[Mo(CO)_2(dppe)_2]I_3$	1.66	[112]
3.	$[Mo(N_2)_2(dppe)_2]I_3$	1.97	[50]
4.	$[PPh_4]_2[Mo(NO)(CN)_5]$	1.93	[47]
5.	$Cs_2[Mo(NO)Cl_4.H_2O]$	1.77	[48]
6.	$[Mo(NO)(o-phen)_2Cl]Cl$	1.68	This work
7.	$[Mo(NO)(bipy)_2Cl]Cl$	1.70	This work

The spin orbit coupling constant (for Mo(I)) is approximately 450 cm^{-1} for t_{2g}^5 configuration The expected magnetic moment value for an octahedral complex would be of the order of 2.3 BM at 300°K [150]. From the above table it is apparent that all the complexes are having magnetic moment value less than that is expected. These low values imply a considerable distortion from the regular octahedral structure for the nitrosyl complexes.

<u>ESR Spectral Study</u>

The ESR spectra of the newly prepared complexes are presented in Figs. 3.28 – 3.30. The room temperature appearance

in powder form

DPPH

$Cs_2\left[Mo(NO)Cl_4 \cdot H_2O\right]$

3.2   3.4   3.6 3.8×10^3 G
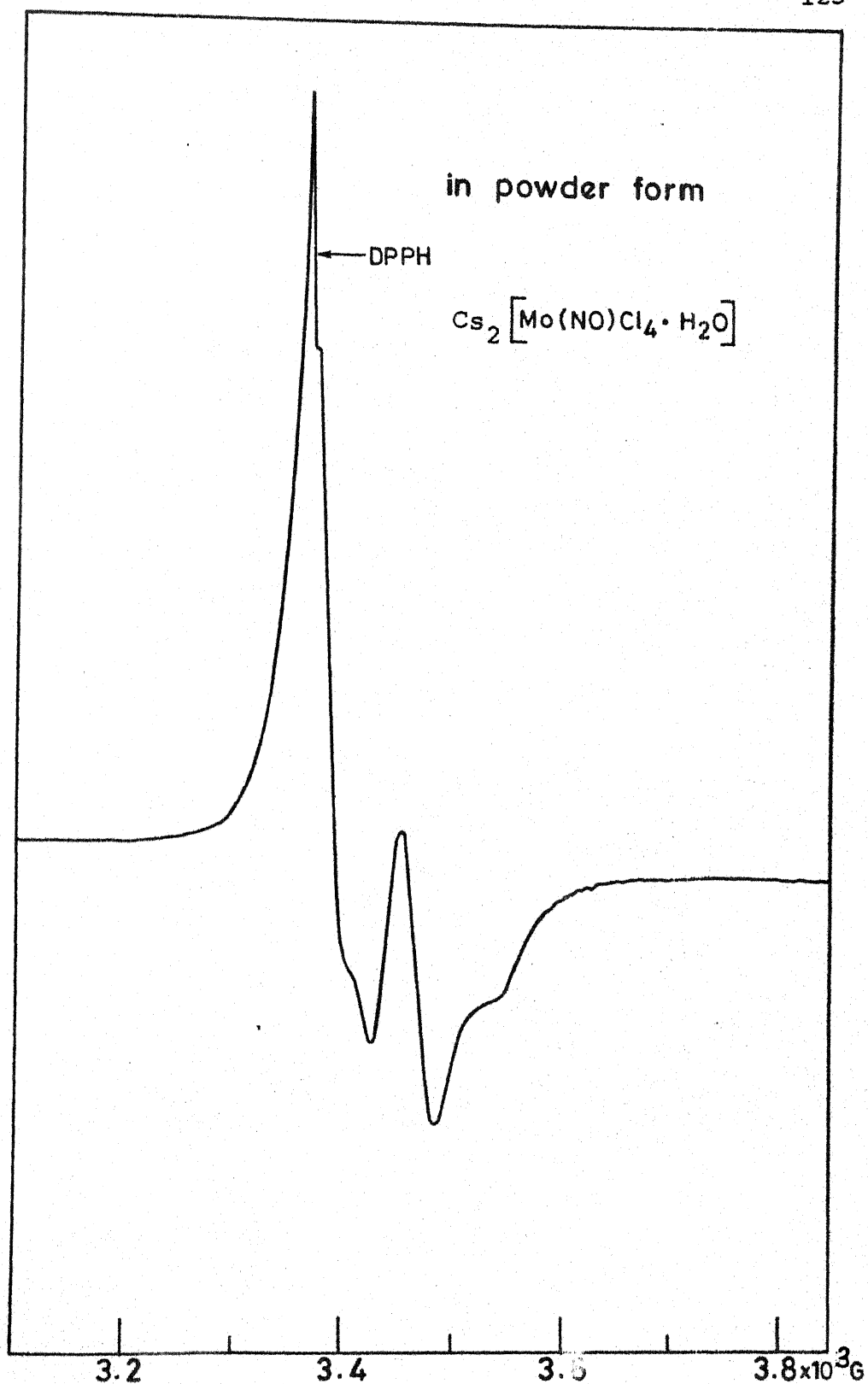
FIG.3.28a   ESR SPECTRUM OF 14.

126

in 6M HCl

$Cs_2\left[Mo(NO)Cl_4\cdot H_2O\right]$

3.2   3.3   3.4   3.5   3.6 ×10³G
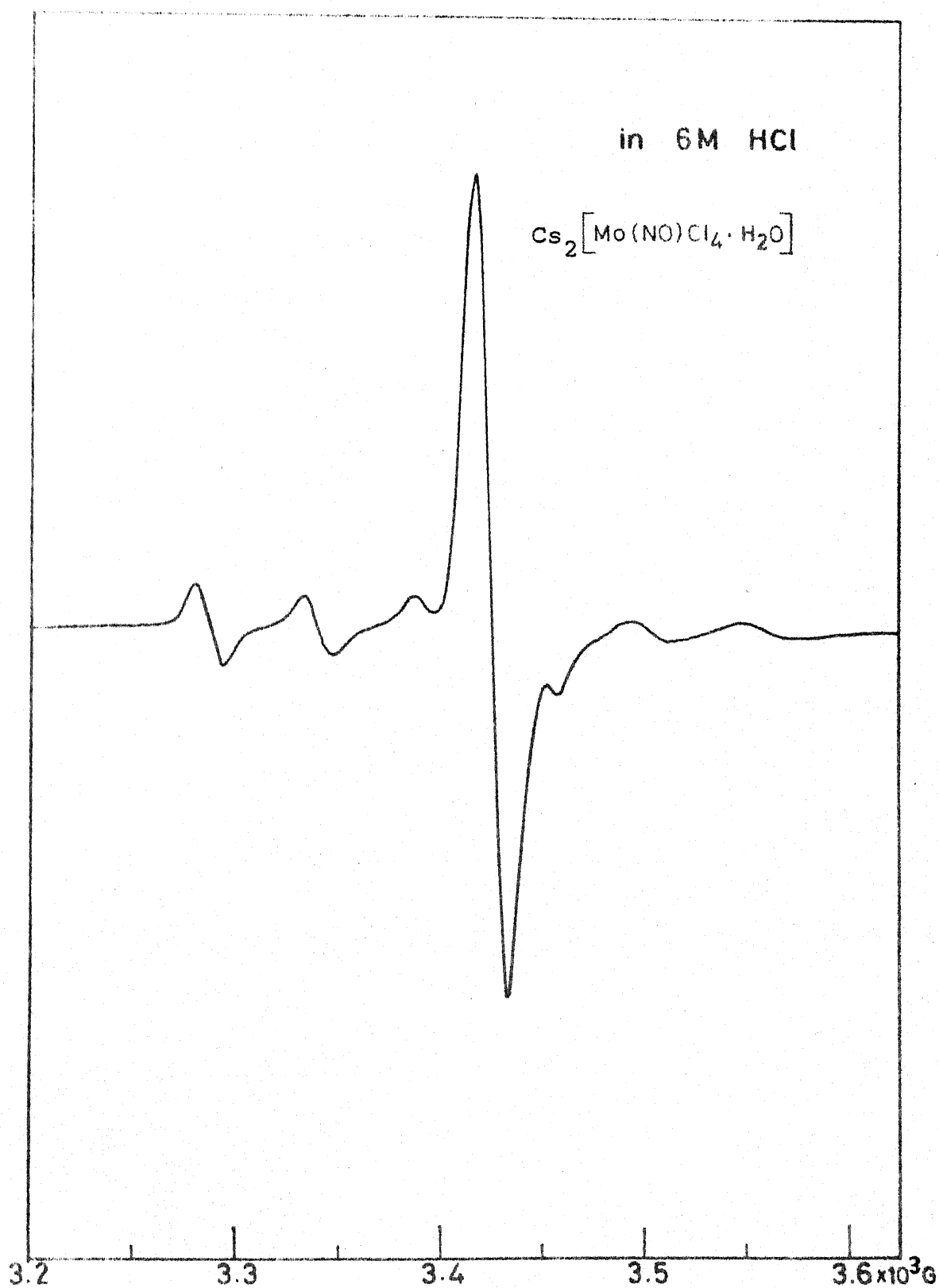
FIG. 3.28b   ESR   SPECTRUM   OF   14 .
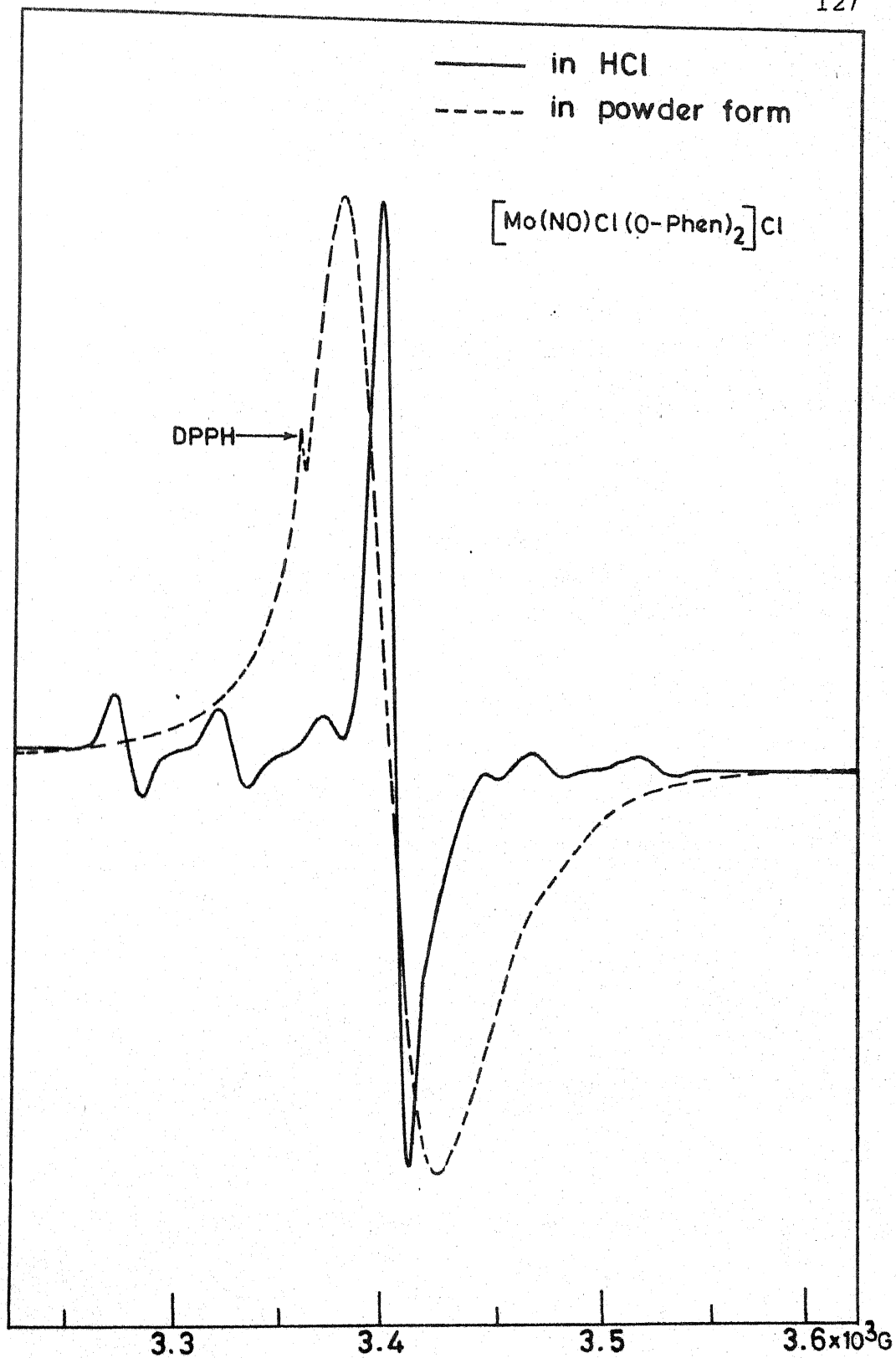
FIG. 3.29   ESR   SPECTRA   OF   **15**.

in powder form

[Mo(NO)(Bipy)₂Cl]Cl

DPPH

3.3   3.4   3.5×10³ G

3.30a ESR SPECTRUM OF 16.

in 6M HCl

$[Mo(NO)(Bipy)_2Cl]Cl$
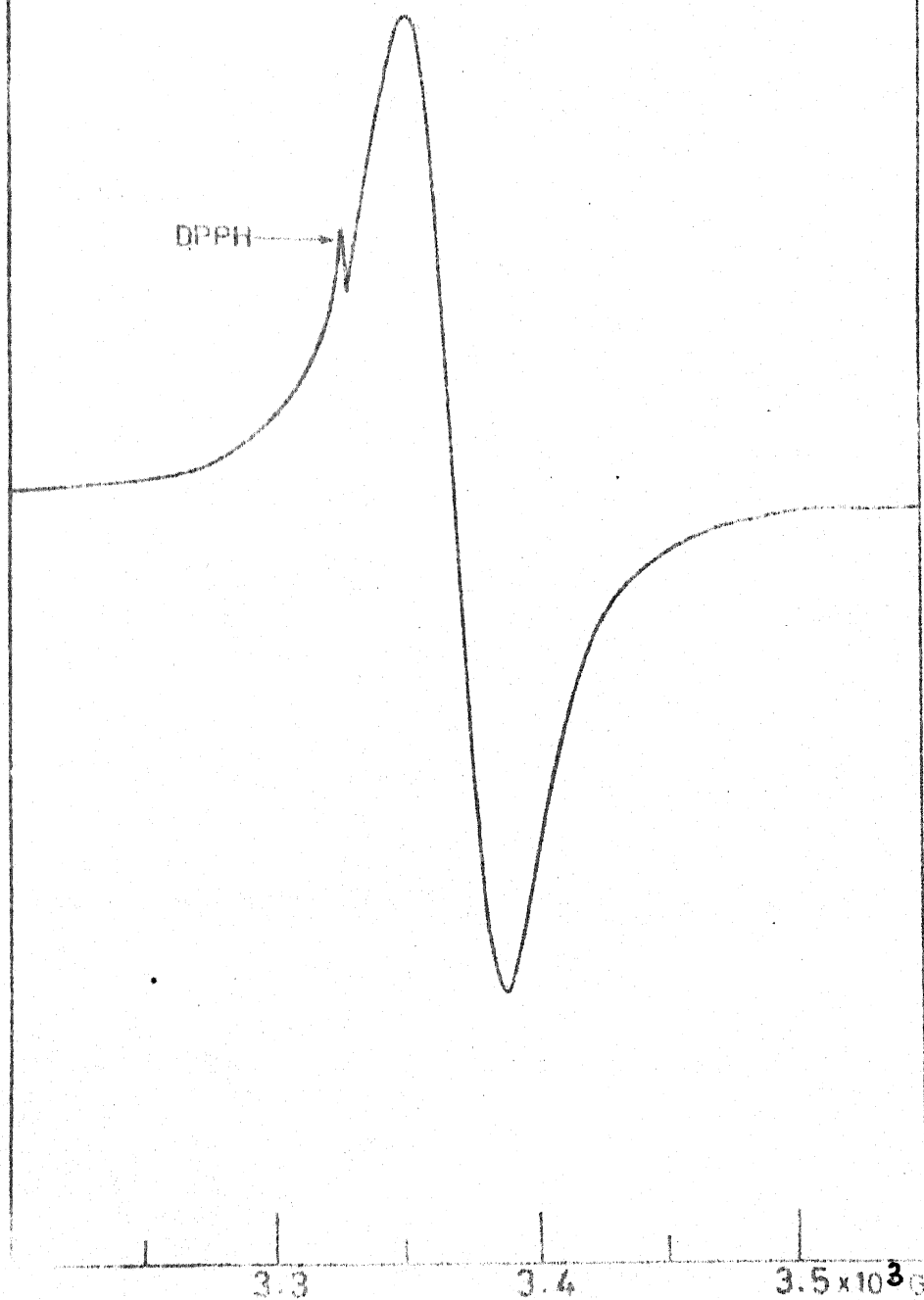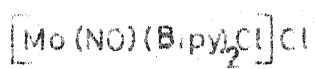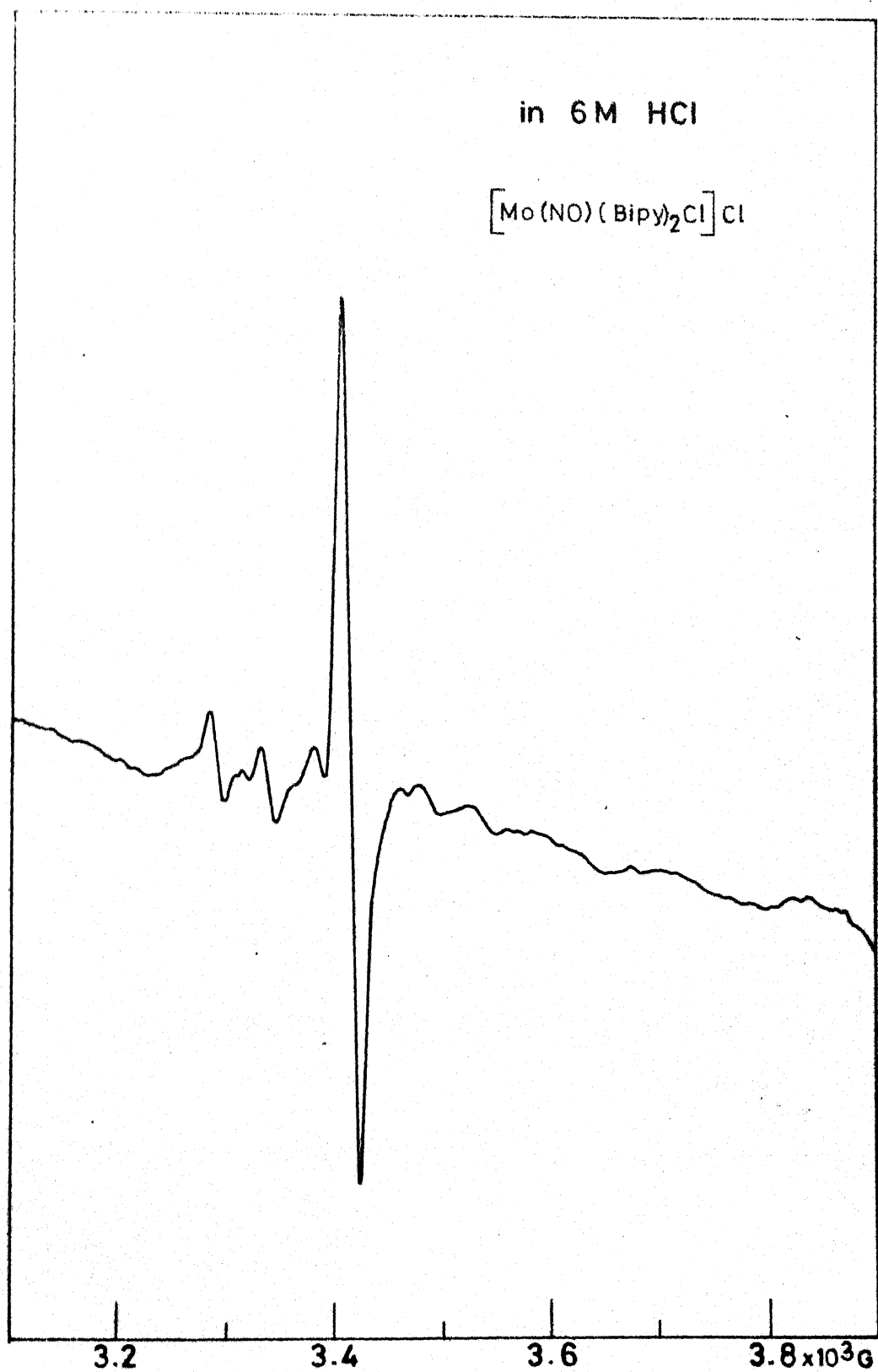
FIG.3.30b ESR SPECTRUM OF 16 .

of these ESR lines along with the anisotropic nature of the
signal suggests a considerable tetragonal distortion in the
complexes. As the g-tensor values observed are in the order
g > g , the unpaired electron must be in the d_{xy} orbital [151].
As expected, no ^{14}N(NO) hyperfine splittings are observed which
is very pronounced in $\{Cr(NO)\}^5$ configurations. The relevant
spectral data are presented in Table 3.7.

<div align="center">Table 3.7</div>

Sl. No.	Compound	In solid phase		In 6 M HCl	
		g	g	$\langle g \rangle_{av}$	$\langle A \rangle$
1.	$Cs_2[Mo(NO)Cl_4 \cdot H_2O]^*$	1.99	1.91	1.96	55 G
		(1.99)	(1.90)	(1.95)	(23.G)
2.	$[Mo(NO)(o\text{-phen})_2Cl]Cl$	1.97	1.92	1.97	50 G
3.	$[Mo(NO)(bipy)_2Cl]Cl$	1.97	–	1.97	50 G

*Values in bracket are taken from the ref. [48].

X-Ray Crystal Data and Structure of $[Ph_4P]_2[Mo(NO)_2(NCS)_4]$

Crystal data of $[Ph_4P]_2[Mo(NO)_2(NCS)_4]$ are presented in
Table 3.8. The unit cell contains four molecules. The struc-
ture of this can be described as an octahedran with the
presence of cis-nitrosyl groups. Both Mo-N distances of the

nitrosyl molybdenum attachment (Mo-N-O) are identical(1.859 Å).
The structure of $[Mo(NO)_2(NCS)_4]^{2-}$ has been reproduced in
Fig. 3.31. The attachment of the nitrosyl groups to molybdenum
is linear and thiocyanates are bonded through nitrogen.

<div align="center">

Table 3.8

Summary of Crystal Data*

</div>

a	12.934 Å
b	12.934 Å
c	31.475 Å
$\alpha = \beta = \gamma$	90.0°
V	5265.4 Å^3
Z	4.0
Density	1.46 g/cm^3 (calcd.)
	1.40 g/cm^3 (exptl.)
Space group	$P4_12_12$ (tetragonal)
Radiation	MoKα ; λ (Kα_1) 0.70926,
	λ (Kα_2) 0.71354 Å,
	graphite monochromator

*Crystal structure analysis was carried out by Professor
Dr. Achim Mueller at the University of Bielefeld, West Germany.
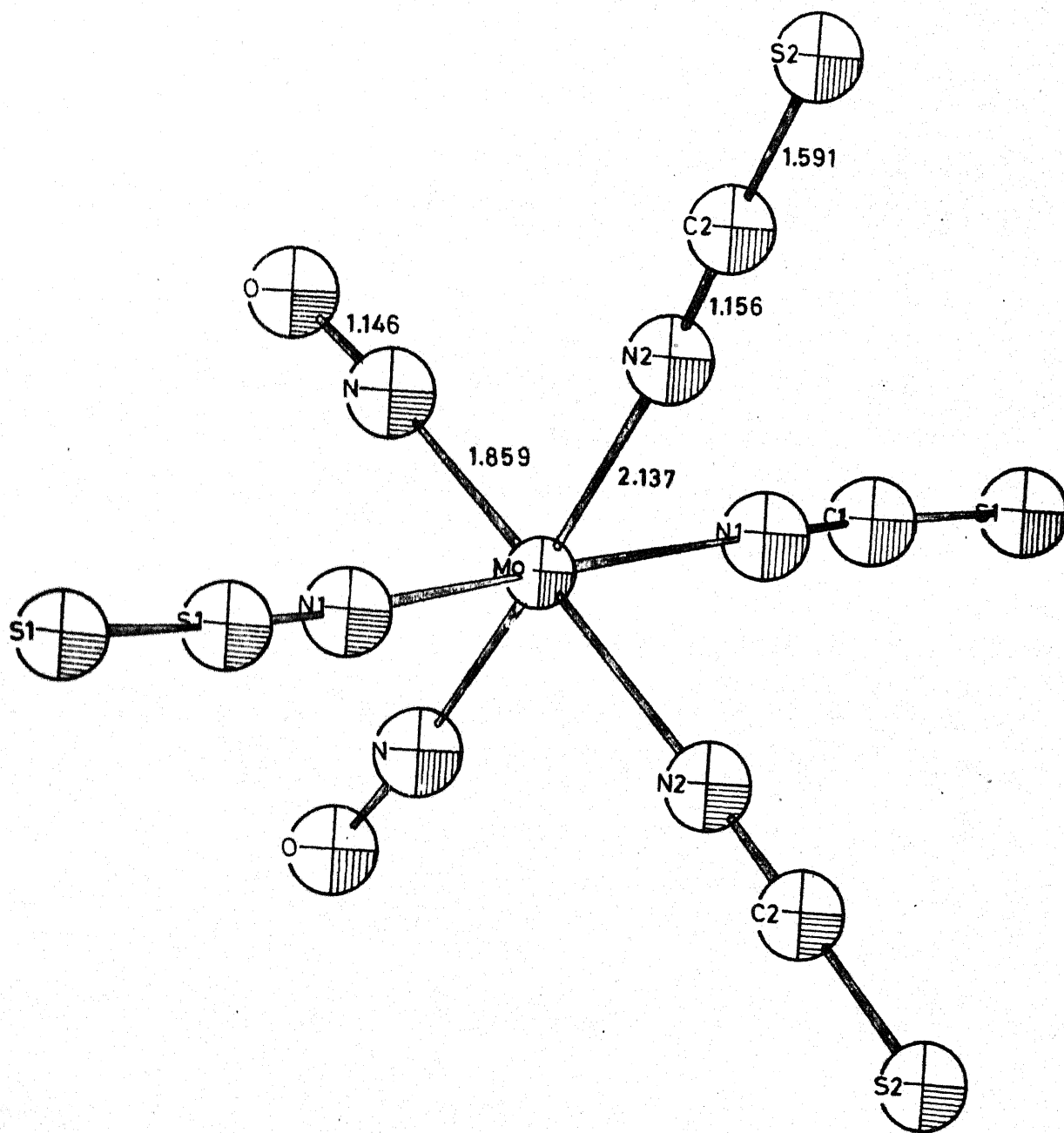
FIG.3.31   MOLECULAR STRUCTURE OF $\left[Mo(NO)_2(NCS)_4\right]^{2-}$

Mechanism of the Formation of $\{Mo(NO)_2\}^6$ Moiety from $\{Mo(NO)\}^4$ and NH_2OH

Nitrosylation reaction of a transition metal compound with hydroxylamine is generally believed to take place in strong alkaline medium whereby hydroxylamine disproportionates to give an unstable 'NOH' which is believed to be deprotonated to generate NO^-. Strong alkali is needed for the deprotonation step. However, the recent findings on nitrosylation of molybdenum as molybdate with hydroxylamine in acidic medium definitely suggests a complicated mechanism. Recent studies on this aspect of the reaction as observed by Wieghardt and coworkers [140] have disproved the earlier suggestion of disproportionation reaction of hydroxylamine and thus the deprotonation of the intermediate NOH. According to them the nitrosylmolybdenum moiety is formed through an intramolecular two-electron oxidation of the coordinated hydroxylamine. The concurrent deprotonation of hydroxylamine occurs along with the intramolecular electron transfer process as:

$$Mo^{VI} + H_2NOH \longrightarrow Mo-NO + 3 H^+$$
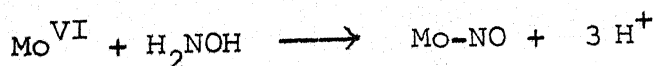
However, the formation of a yellow colour by the reaction of MoO_4^{2-}, and NH_2OH suggests the formation of $\{Mo(NO)\}^4$ moiety [140] instantaneously. The relationship between electron transfer and deprotonation processes is not clear. However, this can be viewed as follows. It has been observed that the same group of workers [140] that when hydroxylamine is used in many fold excess compared to the

molybdate, complexes containing $\{Mo(NO)(NH_2O)\}^4$ configuration are formed instead of simple $\{Mo(NO)\}^4$ moiety. When hydroxylamine in the reaction mixture is not in sufficient excess $\{Mo(NO)\}^4$ group is only formed without the coordinated hydroxylamido(-1) moiety. However, we have observed that when the ratio of molybdate to hydroxylamine is 1:3, hydroxylamidonitrosylmolybdenum moiety is generated. Wieghardt and coworkers [103] have shown that the coordinated $NH_2O(-1)$ group can be further deprotonated to yield $NHO(-2)$ type of bidentate ligands. Thus two successive deprotonation of hydroxylamine with a $\{Mo(NO)\}^4$ group takes place as given below:

$$\{Mo(NO)\}^4 + NH_2OH \xrightarrow{-H^+} \{Mo(NO)(NH_2O)\}^4$$

$$\{Mo(NO)(NH_2O)\}^4 \xrightarrow{-H^+} \{Mo(NO)(HNO)\}^4$$
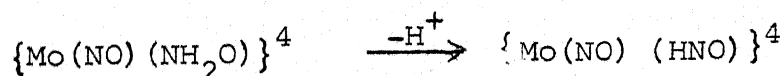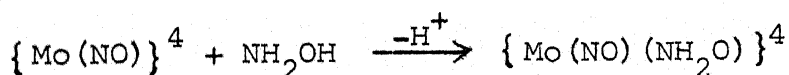
However, it is to be noted that most of the complexes containing bidentate hydroxylamido groups (-1, -2) contain other bidentate ligands. From the stability point of view, it is important to pursue a complex containing $\{Mo(NO)(NH_2O)\}^4$ configuration in presence of monodentate coligand whereby the extrastability (lesser reactivity) imposed by the presence of other bidentate ligands can be minimised. We have already observed that $\{Mo(NO)\}^4$ configuration in the complex $Cs_2[Mo(NO)Cl_5]$ on

disproportionation yield $[Mo(NO)_2Cl_4]^{2-}$. And the instability of $[Mo(NO)Cl_5]^{2-}$ may be due to the presence of a 16-electron configuration which stabilizes on dinitrosylation to acquire an 18-electron configuration. This situation should be different, if we proceed with the mononitrosyl complex $[Ph_4P]_2[Mo(NO)(NH_2O)-(NCS)_4]$ which by virtue of its 7-coordination already satisfies the 18-electron configuration. Thus when this heptacoordinated complex was dissolved in DMF, the yellow solution of the complex slowly turned to green which on addition of methanol resulted in the appearance of a crystalline $[Ph_4P]_2[Mo(NO)_2(NCS)_4]$ in good yield. Interestingly, when the same hepta-coordinated complex is refluxed in acetone medium, a yellow complex is separated as $[Ph_4P]_2[Mo(NO)(ONCMe_2)(NCS)_4]$, the structure of which has recently been determined [108]. The prevention of the formation of a dinitrosyl moiety using acetone has already been shown in the synthesis of dithiocarbamato complexes contain-ing $\{Mo(NO)\}^4$ configuration (vide supra). We have already considered the mechanism by which nitrosylmolybdenum derivatives may function as environmental catalyser (vide Chapter 2.7). Hence we presume that the process of dinitrosylation from $\{Mo(NO)\}^4$ and NH_2OH through two successive deprotonation steps proceeds first without any intramolecular electron transfer. The intermediate $Mo \overset{\text{N-H}}{\underset{\overset{|}{\underset{O}{N}}}{|_O}}$ group should be reactive in the sense that now it contains a lone pair of electrons on nitrogen which is attached to molybdenum and oxygen forming a triangle.

The distribution of this lone pair of electrons in the three membered ring may thus facilitate the removal of H^+ in polar DMF medium. The more electron density thus created on nitrogen atom by this process is probably going to destablize the ring structure whereby a pair of electron is transferred to molybdenum by the cleavage of the Mo-O bond. Thus we conclude that the intramolecular electron transfer takes place only after the complete deprotonation of coordinated hydroxylamine.

CHAPTER IV

SCOPE FOR FUTURE WORK

In nitrogenase molybdenum is attached to iron via sulphur and it is interesting that though molybdenum complexes of dinitogen are known, they are not formed in the presence of sulphur donor ligands. Nitrosylmolybdenum moieties can serve as a model for syntheses of complexes containing sulphur ligands. Interestingly, $\{Mo(NO)\}^4$ moiety can be stablized with a sulphur ligand [154] to give molybdenum cluster compound when the stability is obviously due to its polynuclear aggregate. A simple monomeric unit containing, only one molybdenum would be interesting that they can be interacted with sulphur-containing ligands as coligands and the complex if formed, can be denitrosylated in protic as well as aprotic media.

It is interesting to see that the higher congener of iron, ruthenium is rich in nitrosyl chemistry and the corresponding nitrido complexes are also stable in protic media. The possibility of nitrosyl group transfer from nitrosylmolybdenum to ruthenium and vice versa would be interesting in the sense that in

nitrogenase, whether the bonding site of molecular nitrogen is
molybdenum or iron or both is not known. Protic medium is
important for the execution of such reactions. Whatever
results one may get from such studies, the corresponding
Mo $|$ S $|$ Fe chemistry is going to be interesting to study. The
methodology used in this dissertation would be defnite help
in the investigations mentioned above.

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